FACTORS AFFECTING THE KINETICS OF GELATION OF LIGNOSULFONATE AND THE MEASUREMENT OF THE HEATS OF ASSOCIATION OF TRANSITION METAL COMPLEXES OF ETHYLENE-MALEIC ACID

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PREFACE

This study has two independent parts. Parallel development was used in both parts. All chapters, references, tables, and figures are numbered consecutively.

The first part, consisting of the initial six chapters, is a kinetic study of the gelation reaction of four lignosulfonates. The basis of this analysis is gel time data taken at temperatures ranging from 149 to 232°. In this work statistical analysis techniques were used to determine the lignosulfonate constituents which control the gelation reaction. From the statistical analysis, the reaction orders and the overall activation energy were calculated.

The second part is a determination of the heats of association of transition metal complexes of ethylene-maleic acid. The basis of these heats was the calorimetric data taken at 25°. The entropies of association were calculated using previously determined stability constants and the measured heats reported here. The last five chapters discuss this work.

The author wishes to express appreciation to her advisory committee for their guidance and assistance in preparing this dissertation. Special thanks is expressed to Dr. Neil Purdie chairman of the advisory committee. Other members are Drs. J. Paul Devlin, Tom Moore, and Roger Koeppe.

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CHAPTER I

THEORY AND BACKGROUND FOR LIGNOSULFONATE

Lignosulfonates are unique, multifunctional macromolecular polyelectrolytes. They are derived from the natural polymer lignin, one of the most abundant natural products. Lignin is laid down as a three dimensional network when the surface growth of the tree cell wall has ceased. The composition of lignin, thus the lignosulfonates, differs from plant to plant.[1]

Historical

In 1840 when treating wood alternately with HNO_3 and NaOH, Anselme Payen obtained a product which he called cellulose. From this experiment, he concluded that another material different from cellulose was also removed from the wood. This incrusting material in which the cellulose was imbedded was later to be named lignin. In 1890 Benedikt and Bamber found that lignin contained methoxyl groups. By 1897 Klason advanced the idea that coniferyl alcohol was the building block for lignin.

In 1920 Freudenberg[2] postulated that the monomeric building blocks of lignin could be variations of a structure containing phenylpropane units. He suggested that carbon-carbon or ether linkages would be the principal bonds in the lignin molecule. It took Freudenberg until 1965[3] to determine that the monomers are joined by ether linkages and several types of C-C bonds.

Freudenberg's work helped elucidate the structure and chemistry of lignins. He discovered that softwood lignin consists of guaiacyl propane units linked together in a

variety of ways. He also determined that hardwood lignins contain both guaiacyl and syringyl residues. These hardwood monomers are crosslinked in a variety of ways much like the linkages in softwood lignins. Freudenberg has thus been able to describe the polymerization reactions which form the lignin polymers in plants.[4]

Lignin components such as guaiacyl and syringly are not the only distinctions made in the softwoods and the hardwoods. Other distinctions are that hardwoods are known to contain about 43 weight percent cellulose, 35 weight percent hemicellulose, and 22 weight percent lignin while softwoods contain about 43 weight percent cellulose, 28 weight percent hemicellulose, and 29 weight percent lignin. A further breakdown of the main hemicelluloses shows that xylans and mannans predominate in hardwood and softwood respectively.[5]

Although the main features of the structure have been described, the work of defining the structure of lignin is incomplete even to the present. The lack of complete structural information, however, has not halted the progress of wood chemistry.

Description of Lignosulfonates

One of the oldest applications of wood chemistry is producing pulp by the sulfite process. The industry began in 1866 when a British patent for the sulfite pulping process was issued though it was not until eight years later that the first commercial sulfite pulp mill was opened in Sweden.

During the sulfite pulping process, lignosulfonates are produced simultaneously with cellulose when wood chips are cooked in a digester under conditions of heat and pressure in the presence of a salt of bisulfite and sulfur dioxide. This sulfonation process, which forms the water-soluble lignosulfonates, also breaks down the carbohydrate - hemicellulose - into water-soluble reducing sugars such as glucose, galactose, and mannose.[6,7]

Today, about 1,644 tons per day of 50 weight percent lignosulfonate liquors are

produced as a co-product of the paper industry. The co-product, primarily lignosulfonates, is a coffee-colored mixture of noncellulosic material. It is a water soluble, sub-colloidal, spheroidal molecule which is capable of adsorption on hydrogen bonding surfaces.[8] Lignosulfonate liquor is a blend of high molecular weight polyelectrolytes, wood sugars, and small amounts of inorganic salts such as ammonium or sodium sulfate. It is concentrated to a dark brown, viscous liquor and sold as lignosulfonate. Table I summarizes the classes of compounds in the four lignosulfonates used in this study.

Most of the cellulose, the other major constituent of wood, is not sulfonated by this process. The cellulose in the form of wood pulp is separated from the lignosulfonate by filtration. The cellulose is used in the manufacture of paper and other products.

Molecular Weight Distribution

Polydispersity, a wide range of molecular weight, is a characteristic of non-linear polymers such as amylopectin and glycogen.[13] Commercial lignosulfonates are polydispersive, also known as heterodispersive, with respect to molecular weight.[14] They contain moieties of different molecular structures; therefore, they must be considered as statistical entities, not as a classical chemical compound.[6] The solutions are Newtonian in behavior in concentrations of 40% or more.[8] This behavior is thought to be due to the repulsion of the spheroidal, non-swelling macromolecules.

Bimodal molecular weight distributions for lignosulfonates have been reported by several authors.[15,16,17] The typical molecular weight range for the low molecular weight fraction is from about 100 to 10,000. The typical molecular weight range for the high fraction is about 10,000 to 400,000.[18] From ultracentrifugation and high resolution electron microscopic studies, the average molecular weight of the lignosulfonates is about 50,000.[19,20] Such wide ranges lead to uncertainty in stating a single value of the molecular weight for a given sample. Thus, the polydispersive lignosulfonates are

TABLE I

ANALYSIS OF REPRESENTATIVE LIGNOSULFONATE PRODUCTS

	TREX®LTA Ammonium lignosulfonate from pulp waste[9]	TREX®LTA Ammonium lignosulfonate from pulp waste[10]	TREX®LUA Ammonium lignosulfonate from TREX®LTA[11]	Raylig®-261L Sodium lignosulfonate from pulp waste[12]
Wood blend	100% Softwood	66% Softwood 34% Hardwood	100% Softwood	97% softwood 3% Hardwood
Reducing sugars (%)	19.9	17.7	7.8	12.3
Sulfur (%)	6.8	5.9	6.4	5.2
Nitrogen (%)	3.9	3.6	2.8	3.7
Ash (%)	1.1	0.9	1.6	1.2
Lignosulfonate (Est.) (%)	50-60	50-60	70-80	50-60
Other Carbohydrates (%)	18.3-8.3	21.9-11.9	11.4-1.4	27.6-17.6
pH	3.6	3.3	3.6	3.5

described as being composed of similar polymers but differing widely in molecular weight. As with many other polymer types, lignosulfonates may have molecules that differ as much as 1000-fold in size but can physically interact as one unit with mutual properties.[21]

The polydispersity in the molecular weight of lignosulfonates is accompanied by small changes in physical and chemical properties.[22,23] Examples of those properties which have been found to vary only slightly with molecular weight are viscosity, density, methoxy-group content, u. v. absorption, partial specific volume, and refractive index.

Several authors have studied the methoxy content of lignosulfonate with molecular weight fractions.[24,25,26] The results of each work showed that the methoxy content varied within the narrow range from 10.7 to 14.7 weight percent of each fraction of lignosulfonate.

Rezanowich et al.[27], Markham and coworkers[28], and Yean and Goring[25] found that the u. v. absorption spectra changed only slightly when the weight average molecular weight fractions varied from 19,000 to 52,300.

Markham et al.[28] also studied the partial specific volumes for these molecular weight fractions and found them to be virtually unchanged.

Yean and Goring[29] and Goring and Rezanowich[30] studied the refractive index change with molecular weight and found it to change a maximum of ±5% over the 14 molecular weight ranges studied. Their studies included, in part, weight average molecular weights of 10,000 to 77,000.

Yean and Goring[25] also found that the sulfur content changed from 5.4 to 7.7 weight percent as the molecular weight decreased from 52,300 to 19,000. These similarities allow one to treat the lignosulfonate liquors as entities in the same manner that synthetic polymers such as polyacrylamides or ethylene-maleic acid copolymers are treated.

Current Applications of Lignosulfonates

Even though the chemistry of lignosulfonates is not thoroughly understood, they are used in many commercial ventures. They are surface active agents with the ability to act as dispersants, emulsifiers, chelating or sequestering agents, and binders. They have been used in paints to disperse titanium oxide; in pesticide and dye dispersions; insecticide and wax emulsions; oil-well drilling mud additives; water treatment chemicals; animal feed supplements; soil stabilizers; and road binders.

Statement of the Lignosulfonate Problem

Lignosulfonates are supplied commercially as a dry product or a liquid concentrate containing 50 weight percent solids. They have not, however, been used extensively when controlled gel times are necessary because of product variations of most commercial lignosulfonate streams. These variations may occur when the lignosulfonate liquors are treated with NaOH and KOH, when the products are spray dried, or when the liquors are exposed to oxygen which changes the reducing sugar content. An extensive literature search was conducted to determine if any commercial lignosulfonate products could be found which had a minimum of product variation. The product variation limitation has now been overcome by the selection of particular lignosulfonates that exhibit acceptably uniform properties. The restrictions placed on the lignosulfonates for this study were that the solution pH must be between 2.8 and 4.2, liquid lignosulfonates would be used, and there must be a reproducible reducing sugar content present. Lignosulfonates which met these criteria were TREX® LTA and TREX® LUA (ammonium lignosulfonates, Scott Paper Company) and Raylig® –261L (a sodium lignosulfonate, ITT Rayonier). These solutions are virtually sulfite waste liquors that have not been chemically processed, but that have been concentrated to 50 weight percent solids by evaporation. Each of these lignosulfonate liquors also has a reducing

sugar content which is virtually constant because of the controls during the pulping process.

Lignosulfonates are known to undergo two major gel reactions - gelation which is initiated by high temperatures[31,32,33,34] and crosslinking which is initiated by polyvalent ions such as dichromate[35] or silicate.[36] In this work a kinetic study of the high temperature gelation reaction was conducted. The purpose of the study was to determine the relative importance of the various components of the lignosulfonate liquor which participate in the high temperature reaction.

CHAPTER II

THEORY AND BACKGROUND FOR GELATION

Thomas Graham is usually regarded as the founder of experimental colloid and gel chemistry.[37] The two most important aspects of his theory of gelation are: 1) that there is a sharp gel point; and 2) that in gelled systems a considerable fraction of soluble material still exists.

Definition of Gels

Gels then are defined as non-Newtonian, colloidal systems of solid character in which the colloidal particles constitute a coherent structure. The term gel is used to denote bodies which contain a considerable proportion of liquid, but maintain shape and exhibit rigidity. Electron microscope studies[38] have shown that gels contain large amounts of liquid within a network structure of the colloidal particles. Thus, the gels do not flow as liquids but behave as solids, usually with a very low elastic modulus.

Gels usually consist of two components. These components can be solid-liquid, such as Jello gelatin, or liquid-liquid such as milk, sodium silicate activated by phosphoric acid, and the lignosulfonate gels studied here. The gels resulting from these combinations can be considered as a solution of one giant molecule which consists of macromolecules locally bound together.

The most important property which gives information about the onset of gelation is the increase of viscosity with time. This viscosity increase continues until the solution does not pour. This phenomena is called the gel point. The time it takes to set is called

the gel time.

The gel or solid solution may or may not be easily deformable. Those gels that can be deformed show a yield stress. The existence of the yield stress is interpreted to mean that the gel particles form a continuous network.[39] This network does not allow flow and keeps the solvent enmeshed, that is, the water molecules are held in the hydrated network. This occurs even though the solvent may be as much as 95% or more of the formulation.

Yield stress is present even in gels which have only Van der Waals forces holding the gel together. Gels which have only Van der Waal's forces are called thixotropic gels. Only gentle shaking is needed to break the gel structure and reduce the viscosity so that the gel flows. The gel reforms when the shaking is stopped. A common example of this gel type is catsup.

Gels can also be described as amorphous solid solutions. The more asymmetric the colloidal particles, the lower the concentration necessary to form these solid solutions. Also the longer the particles the fewer of them are necessary to build up a network immobilizing all the solvent.[40]

Types of Gels

Gels are known in great variety because the nature of the gelling material, the dispersion medium, and the nature of the forces which result in the junction points in the network may vary widely. Classifications such as inorganic or organic are made according to the gelling material chemical composition. They can also be classified according to their solvent. Gels with water as the liquid component are hydrogels; gels containing an organic solvent as the liquid are organogels. Gels may be classified as heat-reversible such as gelatin or may undergo a heat-irreversible transformation such as water glass reacting with hydrochloric acid.

The heat-reversibility of gelatin has been demonstrated by X-ray defraction. Above

55^0 the gelatin solution gives an amorphous-type pattern. Upon cooling a crystalline-type pattern develops. When reheating occurs, the crystalline-type pattern disappears coincident with the liquefaction of the gel.[41]

The heat-irreversibility of the water glass-hydrochloric acid reaction is demonstrated by the following experiment. The reaction is initiated by putting the water glass-acid mixture in a temperature bath set at about 35^0. After about one hour a gel forms. Upon cooling the gel does not break as the gelatin gel did. The only way to break the water glass-hydrochloric acid gel, or any water glass gel, is to add NaOH to the gel. After about one hour exposure to NaOH the gel will dissolve.[42]

Xerogels are substances which do not contain a solvent. Freundlich[43] is regarded as the inventor of the term xerogel. The term is used to designate gels which lack a dispersion medium. An example of a xerogel is vulcanized rubber.

Characteristics of Gel Formation

Gels can be formed by chemical or physical crosslinks between polymer molecules, by the association of lyophilic sols, or by chemical reactions such as polycondensation of multifunctional monomers.

Egg albumin is an example of gel formation by a chemical reaction. Upon boiling, the egg albumin denaturates by forming linear colloids. These colloids in turn form a gel which immobilizes the liquid. The vulcanization of rubber is another example of a chemical reaction in which a gel is formed. The double bonds present in unvulcanized rubber are crosslinked with sulfur thus leading to branch points.

Another way gels may be formed is by gelation of lyophilic sols. Gelatin and soaps are examples of this type of gels. The gel is formed by the association of molecules into colloidal particles when the solution is cooled to a super-saturated solution. If the concentration is high enough, the entire solution may be made rigid by the branching and intertwining of the particles. The resulting rigid mass is call a curd. Association gels

are soluble in hot solvents and they set on subsequent cooling. This gel type is characterized by (1) the time of gelation, (2) the gelation temperature, and (3) a low concentration, usually 1 weight percent or less, of the gelling material for gelation to occur.

As described in the previous paragraph, a chemical reaction is not a necessary condition for gelation. Polycondensation reactions which involve two or more reactive sites are well known in polymer chemistry. In this type of gelation, crosslinks and branching points result in the formation of chemical bonds and gel formation. Flory[44] has shown that under certain conditions a polyfunctional condensation leads to formation of a gel fraction which consists of an infinite network. In the course of condensation reactions, a sharp gel point is observed.

The condensation of phenol with formaldehyde in one of the oldest known methods of preparing polymers. These phenolic polymers such as Bakelite have a sharp gel point when they are formed. However, in commercial processes one wants the reaction to proceed as far as possible toward completion without gelation of the reaction mixture in the reaction vessel. In the manufacture of Bakelite resins, the reaction is allowed to proceed in the reaction vessel to the prepolymer called resole. The prepolymer is then allowed to gel in molds.[45]

The lignosulfonates studied here also undergo an unwanted chemical reaction if they are accidentally heat-treated above about 150^0 when the dilute waste liquor is being concentrated in the evaporation unit. Gels can form if the liquors are heat-treated uncontrollably during the evaporation process. Just as the resins formed in the Bakelite process, these gels are very difficult to break. An accident such as this could result in the purchase of another evaporation unit. This is one reason why the high temperature gelation reaction of lignosulfonates needs to be better understood.

Gels can be formed by coagulation or by decrease in solubility. However, it must be emphasized that gelation does not necessarily occur upon coagulation or precipitation of any colloid. For instance, in the coagulation of agar-agar or of gelatin with alcohol, the

colloidal substance is precipitated without immobilizing much of the solvent. Therefore, these two systems cannot be described as gels.[40]

Swelling

Swelling is a characterstic of gel formation that occurs when a xerogel spontaneously imbibes water or some other solvent. When swelling occurs, the gel increases to many times its size. Examples of gels that swell are unvulcanized rubber[46] and agar-agar[40]. Limited swelling occurs when the molecules remain bound in a network while unlimited swelling causes the xerogel to dissolve. Swelling is influenced by temperature, pH, and the presence of salts. The resulting swollen gels can be desolvated by putting them under vacuum causing the gel to shrink as the solvent is evaporated. The gel can swell again when exposed to the solvent. This procedure can be repeated many times. Hysteresis can occur during the drying process but not during the swelling process. The hysteresis occurs if the gels are supershrunk; but during the next swelling cycle, the gels have a 'memory' of their previous swollen state.

Syneresis

Syneresis is another characteristic of gel formation that occurs when gels in which the branch points or crosslinks are not formed by chemical bonds. These gels may rearrange with time causing a shrinkage of the network structure. This shrinkage forces the solvent to be driven out. This extruding of the solvent is called syneresis. The solvent liberation is not the dehydration which occurs upon drying. Syneresis can take place in moist air at low temperatures and is usually promoted by an increase in temperature and the presence of electrolytes.

An example of a gel which exhibits syneresis is water glass and hydrochloric acid. After mixing these two components, the resulting clear solution gels in about an hour at room temperature. Upon gelation the clear solution becomes a blue opalescent solid

which vibrates audibly when it is tapped. With aging, the sodium silicate gel volume shrinks as the water is extruded.[42] The syneresis phenomena has also been applied to biological problems (e.g., tissue dating).[47] Tissues can be dated since younger tissues have a higher water content than older ones just as the newly-set water glass gels have more water than aged gel samples. The 'perspiring' of cheese is also an example of syneresis. Unlike swelling syneresis cannot be reversed.

Gel Formation Summary

The above mentioned examples indicate that gelation is similar to coagulation. It is generally accepted that gelation is a structuration of the system. However, it is difficult to draw a sharp distinction between coagulation and gelation. In general, coagulation is the coalescence of particles without encompassing a significant quantity of the solvent. While in gelation, the particles do not form any compact aggregates, but are joined only at a few points with the solvent bound in the interstitial spaces between the particles.

Gelation of Lignosulfonates

As reported in Chapter I, the lignosulfonate liquors have the ability to gel. The gel reaction is characterized by viscosity increases until a stiff gel is produced. Evidence of this reaction was noted by Crown Zellerbach Corporation in 1956[31]. The controlled gelling of lignosulfonate can be achieved at high temperatures (above about 125^0). This controlled gelling reaction as a function of temperature, composition, and concentration is the basis for the kinetic study described in the next three chapters.

Two authors[16,48] have studied the spent sulfite liquor high temperature reaction in the presence of ammonium bisulfite. Although similar to the high temperature reaction reported here, the reaction was not allowed to proceed until gels formed in the two studies cited, and it was not studied at temperatures other than 150^0. Herrick et al.[16] found that the wood sugars were almost completely eliminated during the heat aging

process. The high molecular weight fraction, which is principally the lignosulfonates, experienced a decrease in average molecular weight as determined by gel permeation chromotography. They have proposed a mechanism in which the wood sugars react with the bisulfite forming sulfonic acid derivatives and are partially oxidized to aldonic acids. This is consistent with the work of Ingles[48] who studied the partial oxidation reaction through the intermediate sulfonic acid derivatives.

Herrick et al.[16] have also proposed that the desulfonation of the lignosulfonate results in the viscosity increase observed. The loss of the sulfonate group from the lignin backbone leads to molecular association of the lignin with other lignin polymers making it less soluble. A viscosity increase was observed in the five lignosulfonates they studied. This is analogous to the four lignosulfonates reported on here which also underwent a solution viscosity increase before gelation occurred.

CHAPTER III

THEORY AND BACKGROUND FOR KINETIC STUDY

General Kinetic Equations

Reaction rates are a function of reactant concentration, reaction temperature, and system pressure. A rate equation can be used to describe the rate of reaction. The rate of a reaction involving chemical species A, B, ..., D can be approximated by two power law expressions.[49] For the reaction

$$aA + bB + ... + dD \longrightarrow \text{Product(s)} \tag{3.1}$$

the power law rate expression can be written as

$$r = kC_A{}^aC_B{}^b....C_D{}^d \tag{3.2}$$

where a,b, ..., d are the orders of the reaction with respect to the chemical species A, B, ..., D and k is the rate constant. This particular form of the rate expression will be referred to as the 'multiplied power law model'.

If the temperature effects are to be studied, an Arrhenius type equation may model the system with

$$k = A \exp(-E_a/RT) \tag{3.3}$$

where k is the rate constant, A is the frequency factor, E_a is the activation energy, R is the gas constant, and T is the temperature.[49]

A transformed equation with concentration and temperature terms combined is given by

$$\ln k = a\ln A + b\ln B + ... + d\ln D + (-E_a/RT) \tag{3.4}$$

where k, a, b, ..., d, A, B, ..., D, Ea, R, and T are defined in equations 3.2 and 3.3 above.

The other form of the power law rate expression describes the following reactions.[49]

$$aA \longrightarrow R \tag{3.5}$$

$$bB \longrightarrow S \tag{3.6}$$

$$\vdots$$

$$dD \longrightarrow U \tag{3.7}$$

where A, B, ..., D are reactant species and R, S, ..., U are product species.

The rate equation is given by

$$r = k_A C_A{}^a + k_B C_B{}^b + \ .... \ + k_D C_D{}^d \tag{3.8}$$

where r is the reaction rate, $k_{A,B,\ ...,\ D}$ are the rate constants, and a, b, ..., d are the reaction orders with respect to the reactants A, B, ..., and D. This is the 'additive power law model'.

In general, rate equations are based on idealized models. A model has some of the attributes of the reaction but there can be deviations from the idealized kinetic models. These deviations could be because of the failure to recognize the contribution from the changing activity coefficients during the reaction or the exclusion of a side reaction which have kinetic significance.[50,51] One can account for some of these changes by using the computer which allows one to change the concentrations of several components concurrently and still be able to determine if a model compares favorably with the observations. Because the lignosulfonates contain several classes of compounds, computer analysis was used to model the system.

Assumptions For Lignosulfonate Study

During this work, the pressure was held constant while the concentration of reactants and temperature were changed. The gel times were observed; they were used as a measure of the appearence of product. An empirical curve-fitting procedure, based on

the rate of reaction being inversely proportional to the gel time, was used to fit the model which describes the lignosulfonate system. The model chosen for this study was derived from a study of the possible variables in the lignosulfonate system.

One assumption in this work is that the same reaction is occurring at all the temperatures studied. This is important if an activation energy is to be calculated. In this model the amount of product was assumed to be constant; therefore the conversion of the reactant is not constant. This means that the gel times are dependent on a certain concentration of product being present in solution before the gel begins to form i.e., the lower the initial concentration the longer the gel time. Also assumed was that the system was a constant density system. This characteristic is important because if the density changes during the reaction volume changes must occur thus complicating the analysis. It was assumed that product was always formed during the heating cycle. If the product began forming at room temperature, the gel time measurements would have to begin when the lignosulfonate liquors were at the pulp mills. This reaction was assumed to be an irreversible reaction. This aspect of the reaction allows for the analysis without any competing equilibrium reactions.

Statistical analysis techniques were used to determine the mathematical model which describes the high temperature gelation reaction. These techniques were employed to analyze the gel time data because the initial lignosulfonate concentration at time equal zero and the final gel time at time equal infinity were the only data measured. The sparseness of data obtained in this study made it necessary to do a trial and error input for the independent parameters used in the model.

Brief Description of Statistical Terms

Some of the basic concepts of statistical analysis such as residuals, standard deviation, covariance, correlation coefficient, and F-distribution are necessary for an understanding of the tests of the models used in this study as well as the inferences gained

from the model study. Throughout this section x_i represents the independent variables, and y is the dependent or response variable.

The residual is defined as the difference between the observed and the calculated value of the response variable y. The residual is designated by $(y - \bar{y})$. The residuals represent the behavior of y that the independent variables don't account for in the model, i.e., the regression equation error in prediction of the response.

The sum of the squares of the residuals are designated by

$$S = \Sigma(y - \bar{y})^2 \tag{3.9}$$

This term is minimized during a least squares regression analysis.

The degrees of freedom are defined as the number of observations minus the number of parameters estimated. For example, if 73 observations are made in a particular set of experiments and a 4 variable plus one constant model is used; the number of degrees of freedom would be (73 - (4 + 1)) or 68.

The variance or the mean square is designated by s^2 and is defined by

$$s^2 = \Sigma(y - \bar{y})^2/n\text{-}p \tag{3.10}$$

where $y - \bar{y}$ is the residual, p equals the number of parameters estimated and n - p is the number of degrees of freedom. The positive square root of the variance is the standard deviation and designated by s.

The measure of the dependence between two variables is the covariance. A high covariance means that an error in the estimate of one variable will cause an error in the other variable. The covariance can be estimated by

$$\text{Cov}(x_1,x_2) = \Sigma(x_1 - \bar{x}_1)(x_2 - \bar{x}_2)/N \tag{3.11}$$

where x_1 and x_2 are variables and N is the number of observations taken during the experiment

A dimensionless measure of the covariance is the correlation coefficient and is defined as

$$\rho(x_1,x_2)\ \text{Cov}(x_1,x_2)/\sqrt{(\text{var. } x_1)(\text{var. } x_2)} \tag{3.12}$$

where ρ is the correlation coefficient between x_1 and x_2, $Cov(x_1,x_2)$ is defined in equation 3.11, and var. x_1 and x_2 are the variances of x_1 and x_2 respectively. A correlation coefficient is a measure of the independence of the variables. It may vary from -1 to $+1$. As the value of the correlation coefficient between two parameters approaches the extremes, the parameters are said to be correlated.[52] [53] That is, a change in the estimate of one parameter will cause a significant change in the estimate of the other parameter. Conversely, if the correlation coefficient between two parameters approaches zero, the variables are said to not be linearly correlated; thus, a change in one should not significantly change the other variable.

The errors reported in the model study are a combination of the errors of the model and the experimental error. Estimates of the errors for the model may be determined by differentiating the model equation with respect to each of the parameters. The resulting equations for these linear models are identical to the normal equations; thus, by inverting the normal equation matrix, an estimate of the variances and covariances for each parameter estimated can be obtained.[54]

Significance probability is defined as a 95% confidence level that the variances being compared are from different populations, i.e., the variables are independent.

An F-distribution analyzes the variance properties of two populations. The purpose of an F-distribution is to determine how well the model accounts for the dependent variable's behavior. The value for the F-distribution is determined by dividing the mean square of one population by the mean square of the other population. Thus, the errors estimated by one model can be compared to the errors of another model.[55] The larger the ratio, the smaller the significance probability, indicating the greater likelihood that one model is a better description of the data.

Computer Programs

Three Fortran computer programs were used to analyze the data taken for this study. The first one was a linear least squares program using the multiplied power law model described above to determine the components in the lignosulfonate which affect the gel times. The second program was a variation of the linear least squares program. In this second program a transformed multiplicative power law model was used to determine the coefficients of the active ingredients in the lignosulfonates. The third program used was a set of statistical analysis programs which plotted the data and calculated an F-test ratio for variable significance. These programs are discussed in further detail in the Appendix.

From these programs the reaction orders were estimated for both the reducing sugars and the lignosulfonate. The activation energy for the gelation reaction was also calculated from a plot of an Arrhenius-type equation.

Linear Least Squares

A multidimensional, linear least squares program called SOLVE was used to determine the independent variables which affect the gel time. This program, as well as all least squares regression analysis techniques, minimizes the difference in the sum of squares of the residuals, i.e., the differences between the variance of the observed and calculated gel times are minimized. It was obtained from the Tulsa Research Center of Amoco Production Company.[54] This program is a general one which allows the independent variables to be squared and can calculate interaction variables from two or more independent variables. An interaction between two or more variables indicates that the magnitude of the effect of one independent variable is affected by one or more of the other independent variables. These higher order features were not used for the analysis on the data studied here because the error associated with determining the in-

itial gel times was in the range of the error determined from the model without the interaction terms.

The program consists of two sections. The first section is the MAIN program. It reads the input data, calculates the appropriate interaction terms, sets up the normal equations, solves the equations by Gaussian elimination, calculates the sum of squares of the residuals, the mean square of the residuals, determines the individual standard deviations and correlation coefficients, and prints the results of the analysis.

In the input section MAIN reads in values of the variables. For example the input variables could be the reducing sugar content, the lignosulfonate concentrations, temperature, and the response variable - the gel times. If one wants to study variable interactions, these interactions are also read by MAIN. The Appendix explains the input procedure for variable interactions.

The second section named MB02AD is called from the MAIN program. This subroutine is a proprietary matrix inversion routine which was obtained from the Harwell Library.[56] It inverts the $X'X$ matrix defined by the coefficients of the terms in the normal equations. The coefficients for the variances and covariances are returned from MB02AD as the terms of $(X'X)^{-1}$.

After the matrix has been inverted, the resultant is then tested for the accuracy of the fit by comparing the estimated gel times with the input gel times. The correlation coefficients are calculated for each pair of variables including all variable interactions and squared terms.

SOLVLNL is another form of the linear program SOLVE. SOLVLNL was used to determine the coefficients for the independent variables utilizing a linearized form for the lignosulfonate gelation model. With the exception of the temperature term which is converted to 1/temperature ^{0}Kelvin, SOLVLNL takes the natural logarithms of the input variables. The results of this analysis are summarized in Chapter V. The results from SOLVE and SOLVLNL were used as input for the Statistical Analysis System programs

described below.

Statistical Analysis System

The SAS programs can perform regression analysis, do special statistical tests, and plot data. These programs were purchased from the SAS Institute, Chapel Hill, North Carolina. The SAS programs were used to plot the data rather than to do the model development because the SOLVE and SOLVLNL programs have a more efficient and more accurate matrix inversion technique. The plots generated by SAS graphically displayed the results of the SOLVLNL program. From the slopes of the lines on these plots, the reaction orders for the reducing sugars and the lignosulfonate were determined.

One of the SAS programs was used to calculate the F-test ratio to determine the significance of the variables in the model. The results of these analyses are given in Chapter V.

CHAPTER IV

EXPERIMENTAL FOR LIGNOSULFONATE STUDY

Equipment

Reaction Cells

The reaction cells (Figure 1) were stainless steel cylinders approximately 24 cm high and 1.2 cm in diameter with a volume of 14 ml. The bottom ends of the cylinder were sealed with a stainless steel cap. A stainless steel spacer was inserted in the reaction vessel. A steel ball (0.51 cm in diameter weighing 4.18 gm), free to rise and fall within the cylinder, was placed in the reaction vessel on top of the spacer. A second stainless steel cap fitting containing a 0.3 cm steel pressure line was used to seal the upper end of the cylinder. Each reaction vessel was pressure tested to 680 atmospheres at 278°.

Reaction Oven

The high temperature reaction oven used was an Isotemp (Fisher Scientific Company) modified to accept 10 reaction cells simultaneously. The modification consisted of drilling ten 3 cm in diameter holes in the top of the oven. Each reaction vessel was manifolded to a nitrogen bottle. A back pressure regulator manufactured in the Amoco Production Company Research Laboratory machine shop was used in the system to maintain the system pressure. The pressure gauges on the oven manifold and the back pressure regulator were manufactured by Marsh Instrument Company. A stainless steel vessel (9 cm x 2 cm) manufactured by Amoco Production Company Research Laboratory machine shop was mounted outside the oven as an overflow vessel.

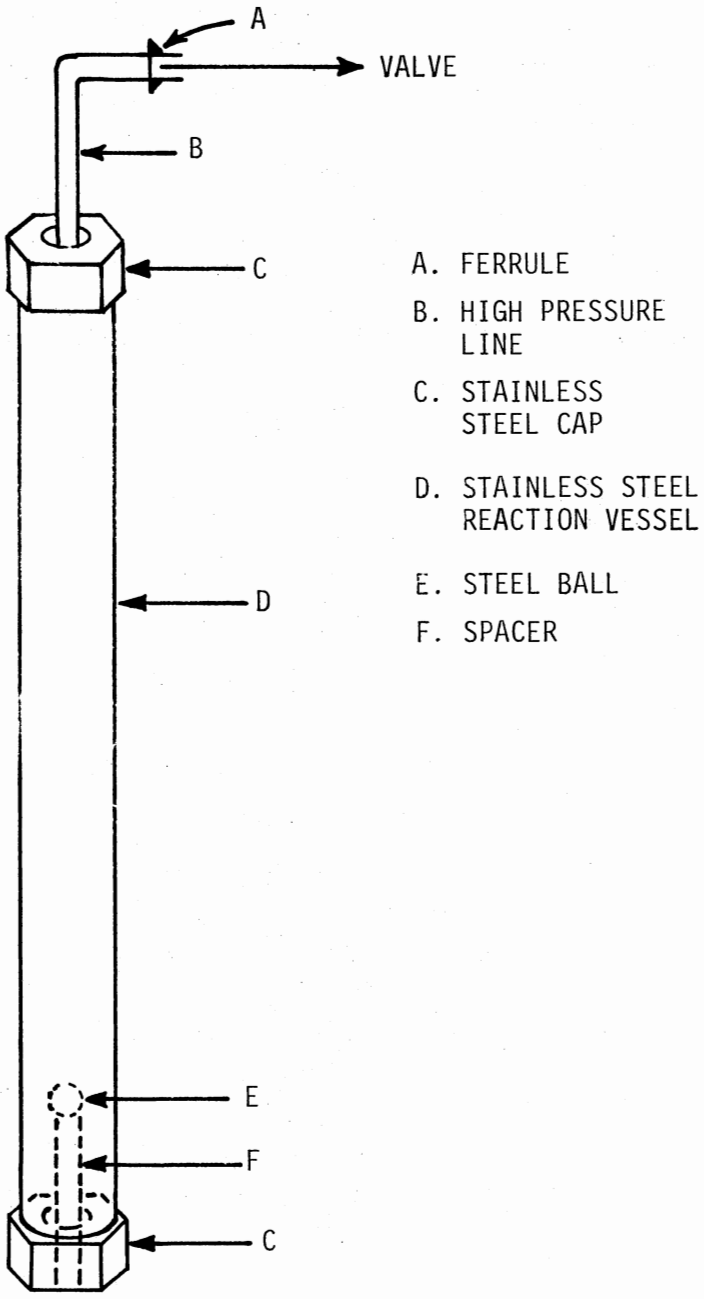


Figure 1. Reaction Cell for Lignosulfonate Study

Procedure

Solution Preparation

In all cases a predetermined amount of the commercially available lignosulfonates and distilled water were weighed separately on a Mettler balance (Model P1200). The two weighed samples were hand mixed at room temperature. Approximately 10 ml of the solution were placed in a high temperature reaction cell. This allowed sufficient volume for expansion of the solution when heated.

Gel Time Measurements

After loading the reaction cylinder, it was charged with nitrogen to a pressure of 48 atmospheres. The cylinder was then loaded in a vertical position in the pre-heated, air-circulating oven described above and manifolded to the nitrogen source with the back pressure regulator in line to maintain the desired system pressure. Mounting all the reaction cells usually took an elapsed time of about 10 minutes. The time required to mount the reaction cells and to heat the solutions was negligible with respect to the time required for gelation to occur. The timing for the gel began after the cells were mounted and manifolded. As the reaction proceeded, a magnet was used to lift the steel ball off the bottom of the cylinder. A mechanic's stethoscope was used to detect the ball reseating at the bottom. Failure to hear the impact indicated gelation of the solution, i.e., the gel was sufficiently rigid to resist the passage of the steel ball. At such time, the cylinder was removed from the oven, cooled, depressurized, and opened to visually confirm the presence of a gel. The cooling step took approximately 1 hour. This procedure was used to generate the gel time curves at temperatures ranging from 149-232°. These gel time curves are the basis of the kinetic study.

CHAPTER V

EXPERIMENTAL RESULTS AND DISCUSSION FOR LIGNOSULFONATE STUDY

The results discussed in this chapter show that the gel time data can be used to determine the components in the lignosulfonate liquor which influence the kinetics of the high temperature gel reaction.

Gel Time Curves

Two physical properties of these gels were studied. A Brookfield Helipath viscometer was used to determine the gel viscosities. This viscometer is driven vertically in a helical pattern such that a different path from top to bottom and bottom to top is taken through the gel to measure the viscosity. The viscosity measured was greater than 3,333,000 cp, the limit of the instrument, for the gels with a lignosulfonate weight fraction of 0.05 or greater.[32] A sample gel was also submitted for x-ray diffraction analysis. It was found to be an amorphous solid.[57] These results show that the gels are strong, non-flowing solids even though they are amorphous.

The gel time data presented in figures 2 thru 5 is the time it takes for the solution viscosity to build until gelation occurs. The error bars on the gel time curves represent the probable error in the observed gel time. If an error bar is not included on the point, the error was less than the diameter of the circle chosen to represent the observed gel time.

The probable error for all the gel times observed was determined by the difference between the time of the last reading taken before gelation and the gel time observed.

This error analysis technique was used because the gel could have set immediately after the reading before gelation or just before the reading designated as the gel time was being taken.

The gel time data used in this study were determined to be acceptable from the estimate of the probable error for the observations. The average of all the errors in the gel times was 11%. The maximum experimental error was 21% with the minimum experimental error equal to 1.7%. Because the probable error in the gel times was reasonably low, the data was used as input for the statistical analysis programs and for determining the reaction orders and the activation energy.

Oconto Falls TREX ® LTA

The first lignosulfonate studied at high temperatures was TREX®LTA, an ammonium lignosulfonate, processed by Scott Paper Company at the Oconto Falls, Wisconsin, pulping mill. The lignosulfonate produced at Oconto Falls has a pulping mix containing a hardwood-softwood ratio of 34/66. The reducing sugar content as a result of the pulping process was 17.7 weight percent of the total solution active ingredients.[10]

Figure 2 shows the effect of temperature on gel time over a range of lignosulfonate concentrations and temperatures for the irreversible high temperature reaction of Oconto Falls LTA. The gel times vary inversely with temperature and concentration at 149, 163, 177, and 191°. For example, at 149° the gel time of 0.06 weight ratio LTA is 505 hours. But at 177°, the respective gel time is 79 hours. Both of these gels and all the gels formed were solid with no free water. Table II summarizes the Oconto Falls gel time data.

Everett TREX®LTA

When the pulping mill of Scott Paper, located in Everett, Washington, was put into production, samples of Everett TREX® LTA were obtained. It differs from Oconto

Falls TREX® LTA in that it is pulped from 100% softwood and has a reducing sugar content of 19.9 weight percent of the total solids content.[9] Figure 3 displays the gel time curves generated by the Everett TREX ® LTA at temperatures of 149, 177, 204, and 232°. The gel times observed are longer than those of Oconto Falls LTA (Figure 2) at comparable temperatures. For example, Everett LTA at 0.07 weight fraction and 177° gelled in 94 hours while Oconto Falls LTA at comparable conditions gelled in 71 hours. As in the case with Oconto Falls high temperature gels, all the gels formed are very firm. Table III summarizes the Everett LTA gel time data.

TABLE II

OCONTO FALLS TREX ® LTA GEL TIME DATA*

Soln. Conc. (Wt. Fract.)	Gel Time (Hrs.)** 149°	163°	177°	191°
.05	590	223	83	37
.06	505	185	79	35
.07	440	175	71	31.5
.08	390	165	65	37.5
.09	360	160	54.5	24.5
.10	305	148	53	22

* Reducing sugar 17.7 wt. % solids.
** All reactions performed at 48 atm.

TABLE III

EVERETT TREX® LTA GEL TIME DATA*

Soln. Conc. (Wt. Fract.)	Gel Time (Hrs.)** 149°	163°	177°	191°
.04	a	a	20	4.2
.05	800	115	18	3.9
.06	630	104	16.5	3.6
.07	535	94	a	3.4
.08	485	88	14.5	3.3
.09	450	83	14	a
.10	425	80	13.5	3.0

* Reducing sugar 19.9 wt. % solids.
** All reactions performed at 48 atm.
a Means no solution tested

Everett TREX® LUA

Everett TREX® LUA is an experimental lignosulfonate fractionated from a commercial LTA sample. The LUA was pulped from 100% softwoods and has a reducing sugar content of 7.8 weight percent solids. The low reducing sugar content is a result of the fractionation process. The lower molecular weight lignosulfonates were also removed during the fractionation.[11] The LUA gel time curve at 191° is shown on Figure 4; examples of the gel times observed were 82 and 76 hours for 0.06 and 0.10 weight ratio respectively. These gel times compare with the Oconto Falls 191° gel times of 35 and 23 hours respectively. These gels had a firm consistency when touched just as the

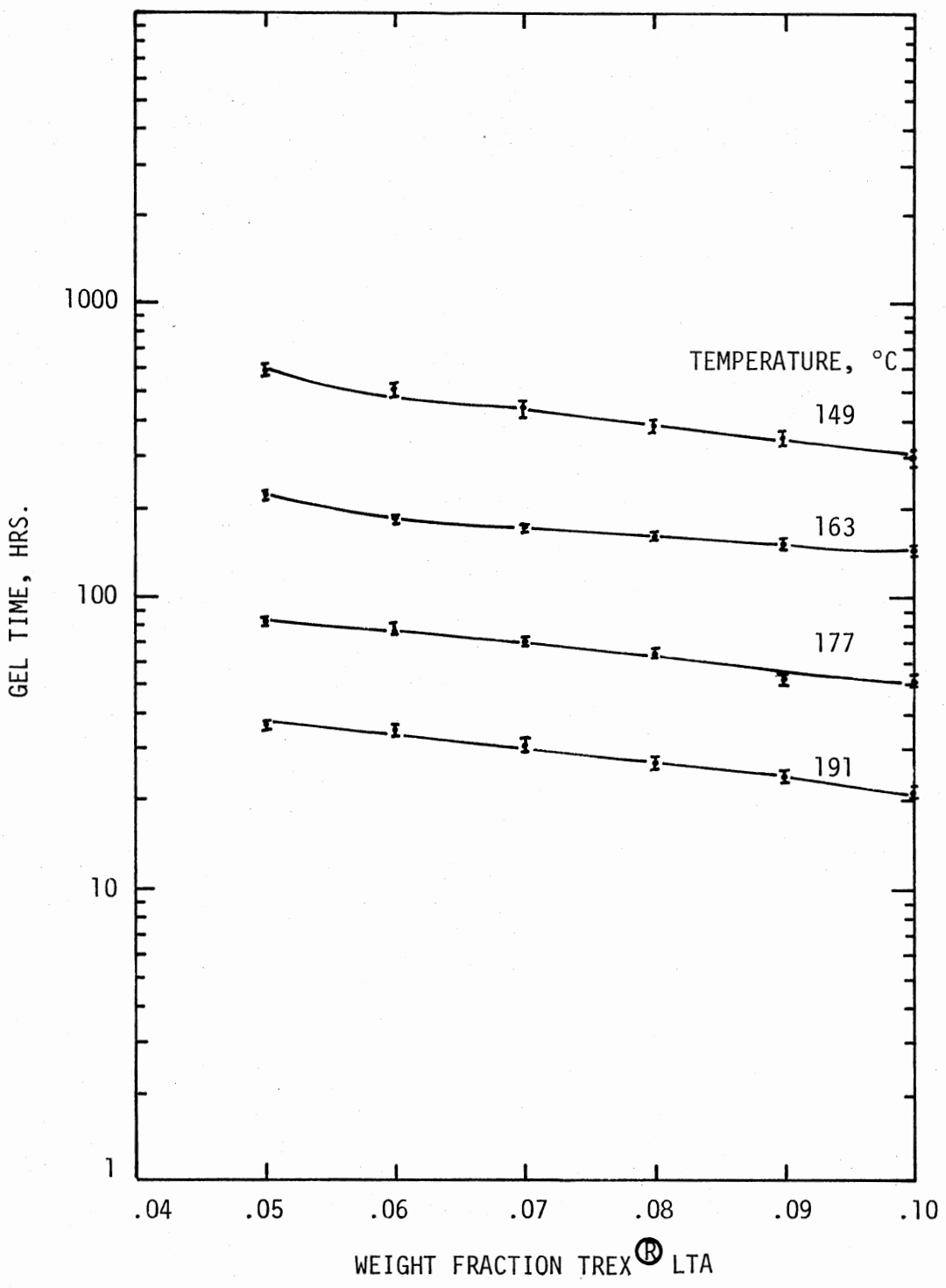


Figure 2. Temperature Dependent Gel Time Curves for Oconto Falls TREX® LTA

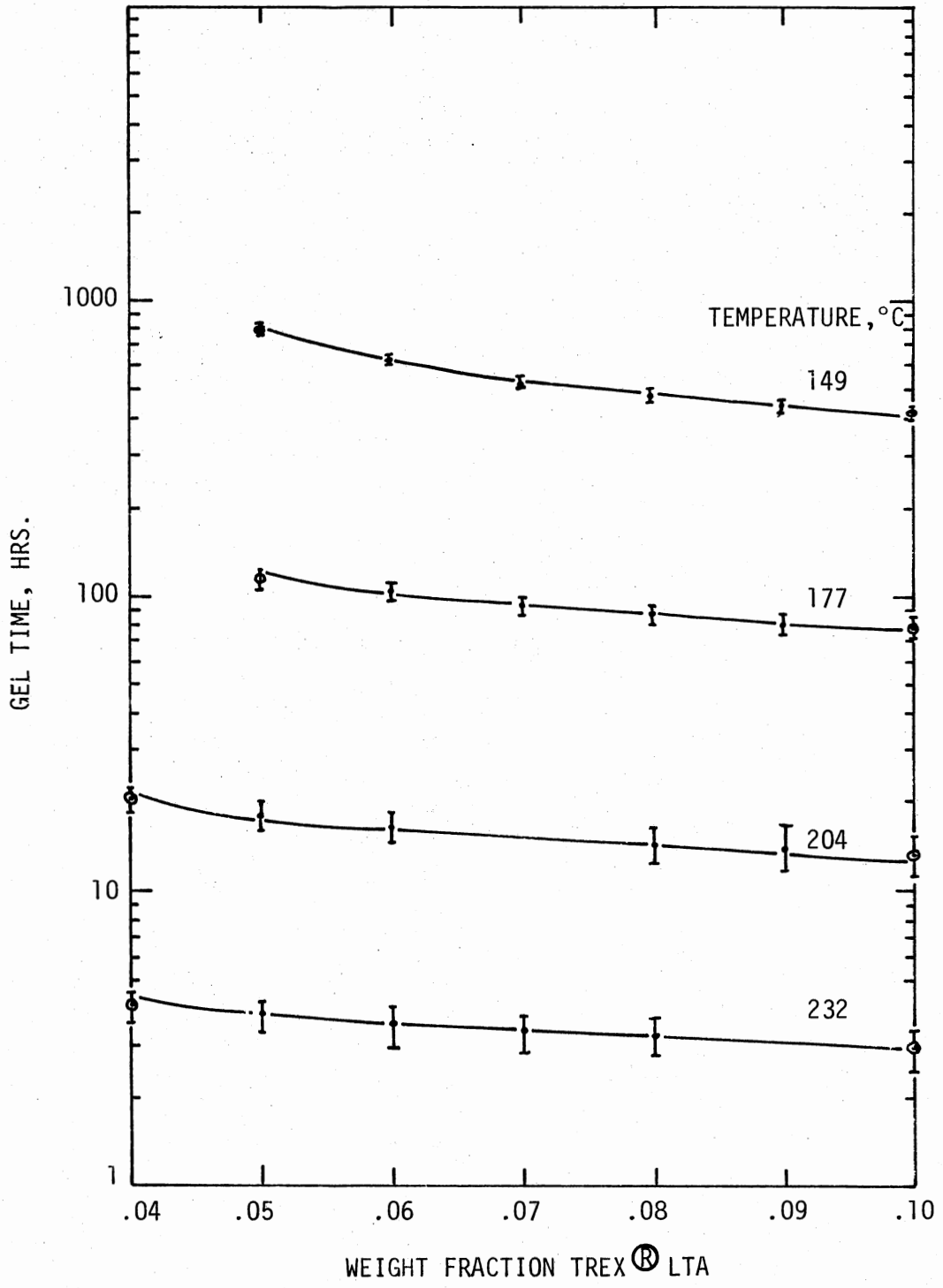


Figure 3. Temperature Dependent Gel Time Curves for Everett TREX® LTA

other gels described previously. Gel time curves at other temperatures were not determined because the total experimental sample available was approximately 100 ml. which was insufficient for testing at other temperatures. The LUA gel time data are summarized in Table IV.

TABLE IV

EVERETT TREX® LUA GEL TIME DATA*

Soln. Conc. (Wt. Fract.)	Gel Time (Hrs.)** 191°
.04	85
.05	83
.06	82
.08	80
.09	78
.10	76

* Reducing sugars 7.8 wt % solids.
** All reactions performed at 48 atm.

Raylig® -261L

Raylig® -261L, also designated as Raylig, is pulped from 97% softwood and 3% hardwood and has a reducing sugar content of 12.3 weight percent of the solids.[12] It differs from the LTA's and LUA in that it is a sodium lignosulfonate, not an ammonium lignosulfonate. The gel time curves produced from the diluted Raylig at temperatures of

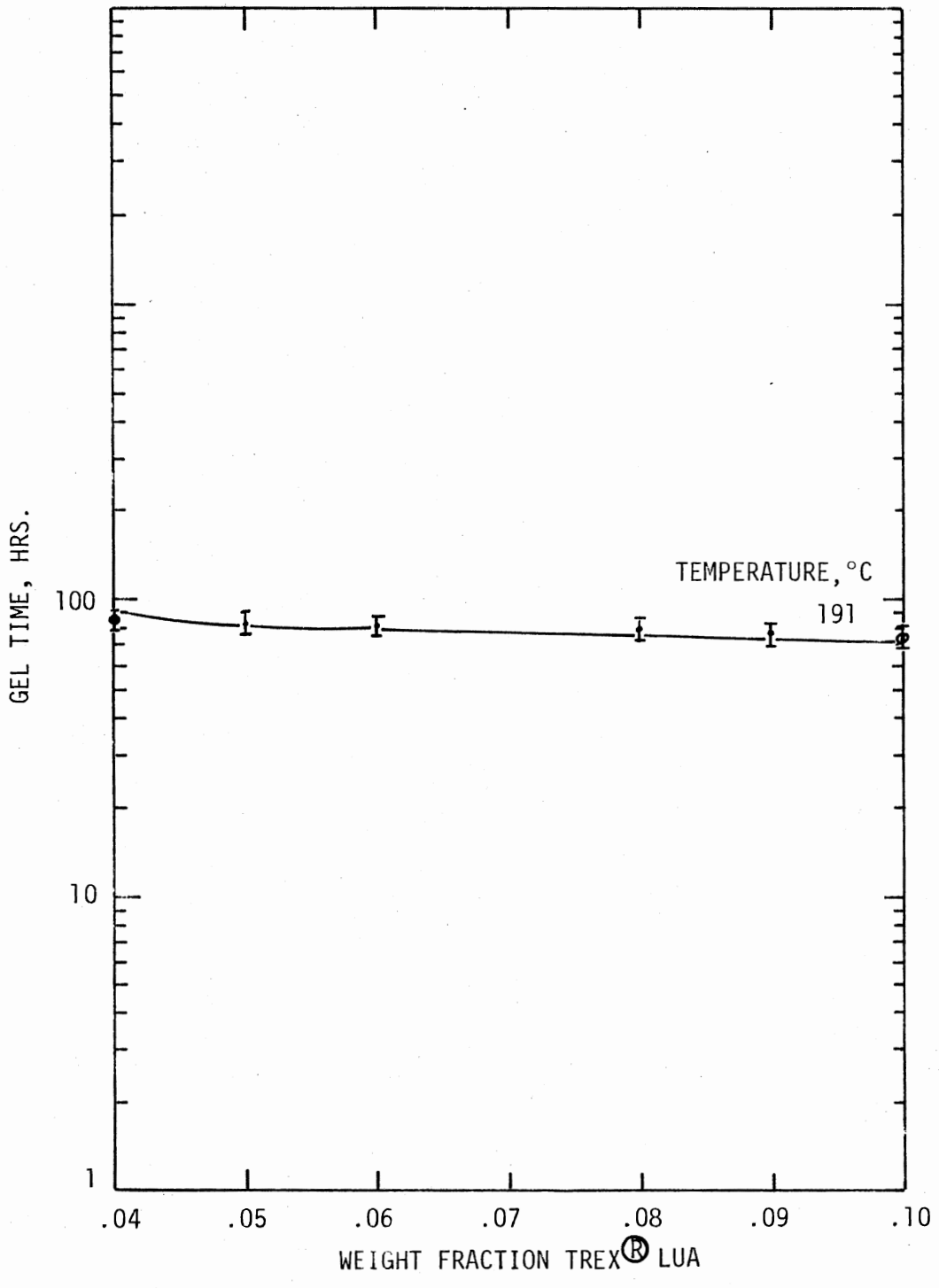


Figure 4. Temperature Dependent Gel Time Curves for Everett TREX® LUA

191, 204, and 232° are shown in Figure 5. Table V summarizes the Raylig gel time data. All the gels produced were firm, and the gel times were considerably longer than those observed for LTA. For example, the gel time for 0.05 weight fraction Raylig was 100 hours at 191° while the corresponding gel time for TREX® LTA produced at Oconto Falls was 37.5 hours. At 204° 0.08 weight ratio Raylig had a gel time of 26.5 hours while Everett LTA gelled in 14.5 hours at comparable conditions.

TABLE V

RAYLIG® -261L GEL TIME DATA*

Soln. Conc. (Wt. Fract.)	Gel Time (Hrs.)** 191°	204°	232°
.04	135	35	a
.05	100	32	7
.06	86	30	6.3
.07	76	28.8	5.7
.08	72	27	5.2
.10	62	24	4.5

* Reducing sugars 12.3 wt. % solids.
** All reactions performed at 48 atm.
a Means no solution tested

Building the Kinetic Model

Hammett[58] has conducted a study of mixtures of drag reducing polymers in distilled

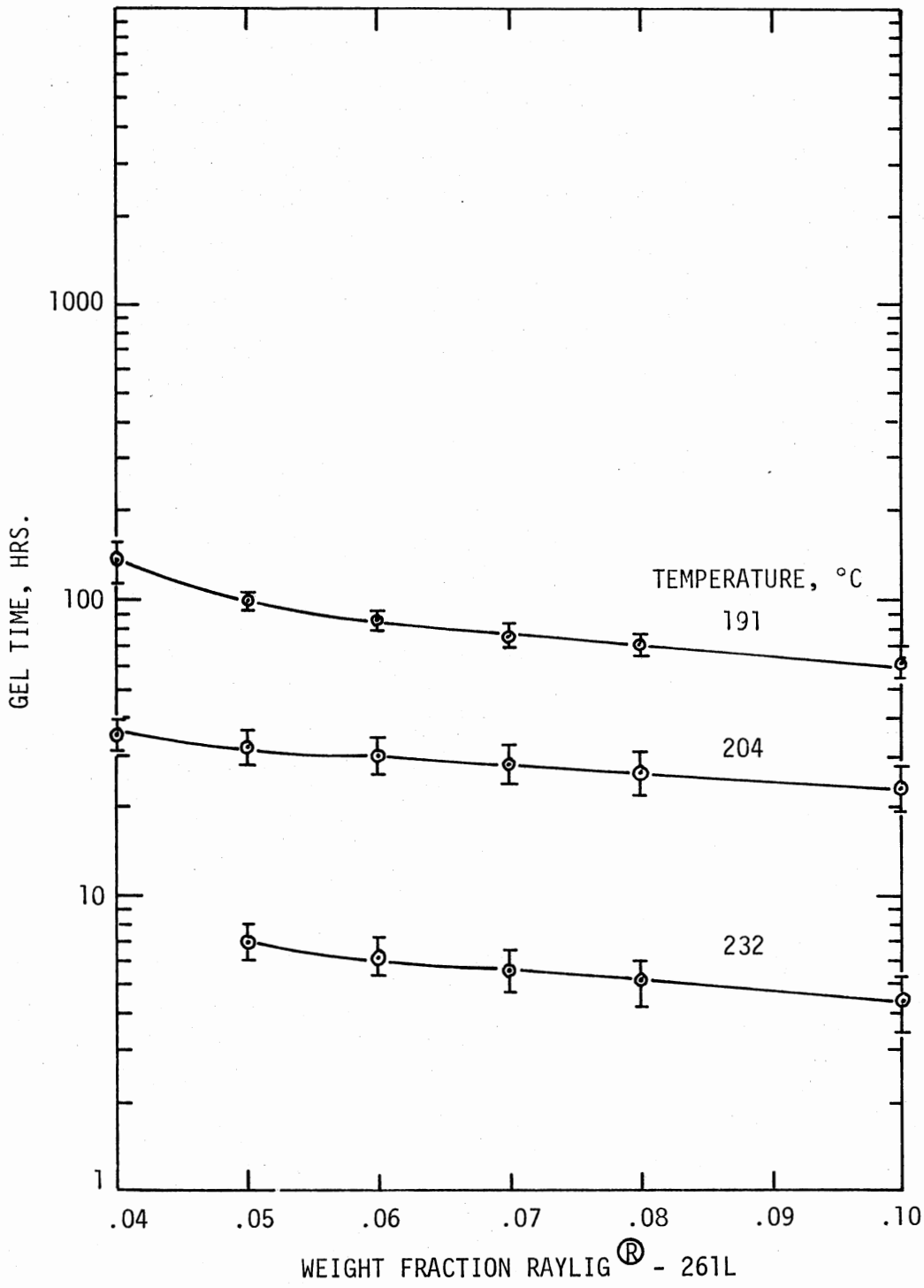


Figure 5. Temperature Dependent Gel Time Curves for Raylig® - 261L

water. In his work several pure drag reduction polymers were studied then mixtures of each of these drag reducers were studied. A non-linear model was designed which described his observations.

Determining the Independent Variables

In this study the mixtures of chemicals were already present because lignosulfonates are composed of three major types of compounds and two elements. These classes of compounds are reducing sugars, lignosulfonates and other carbohydrates while the elements are sulfur as sulfites, and nitrogen. A trial and error approach was used to determine which variables from the five major components in lignosulfonate were independent. By using different combinations of these five types of compounds with the statistical analysis program called SOLVE, the classes of compounds which controlled the gelation reaction were determined.

Figures 6, 7, and 8 are bar graphs which show some of the results of this analysis. In each of these figures, the y-axis is the absolute value of the correlation coefficient. The horizontal line at 0.5 is included for reference because variables are defined to be independent when the correlation coefficients are less than 0.5. The x-axis shows some of the variables used in the study.

Figure 6 shows the high correlation coefficients for a seven variable model in which the variables were softwood in the pulp, softwood sugar content, hardwood sugar content, lignosulfonate weight fraction, sulfur weight fraction, and nitrogen weight fraction. Using these variables eight correlation coefficients were greater than 0.5 which means that these variables were dependent. The largest correlation (0.92) occurred between the hardwood sugar content and the temperature. The smallest correlation (0.51) shown is between the sulfur weight fraction and the softwood in the pulp, however the smallest correlation coefficient calculated (0.03) was between the hardwood reducing sugar and the temperature indicating that these two variables are independent of each

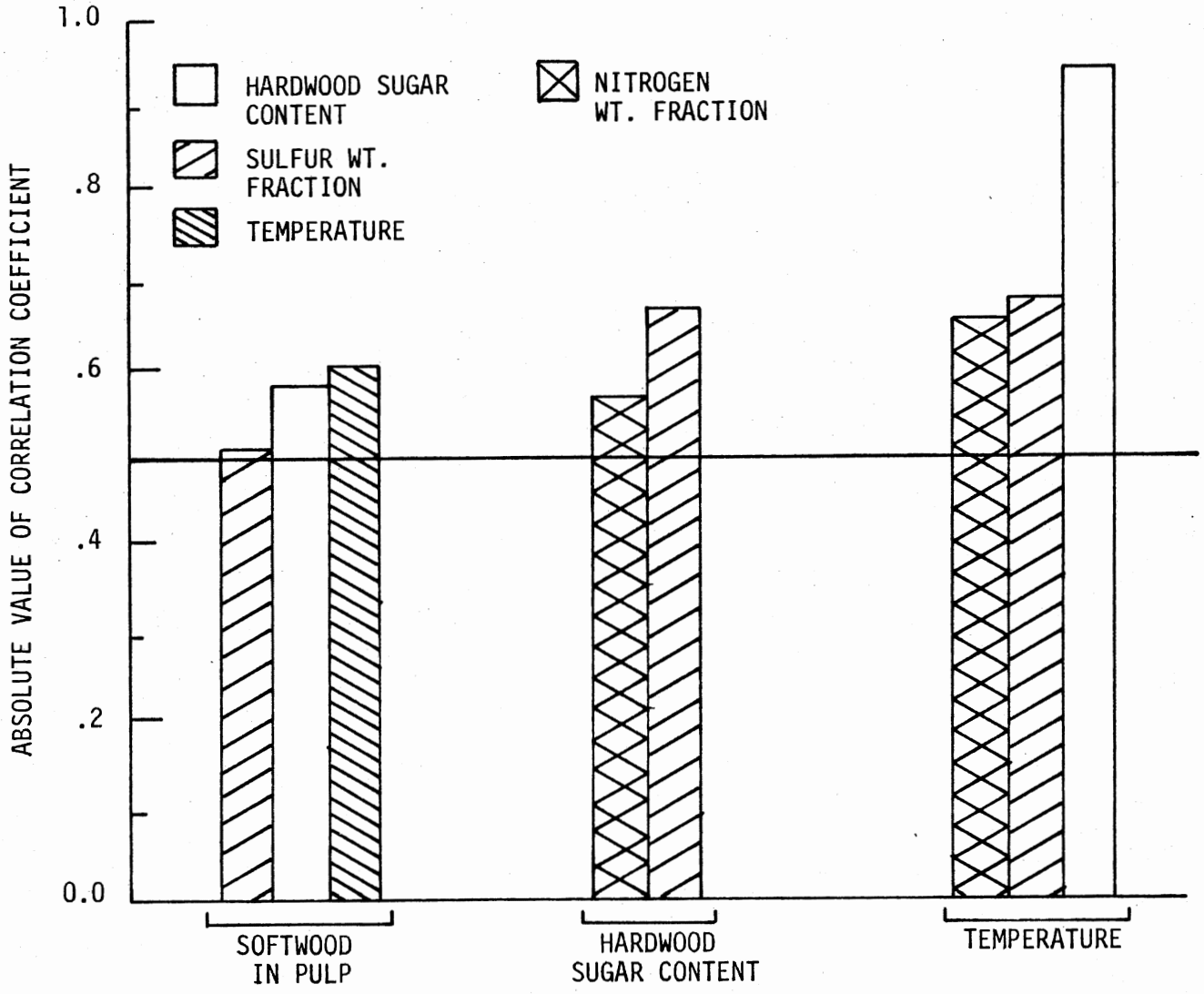


Figure 6. Examples of Correlation Coefficients for Seven Variable Kinetic Model

other. Several other cases were studied to determine the independent variables.

Figure 7 shows some of the correlation coefficients calculated using a five variable model. The variables studied were the temperature, the softwood sugar content, the hardwood sugar content, the lignosulfonate weight fraction, and the softwood in the pulp. Two correlation coefficients (softwood in the pulp correlated with the hardwood and softwood sugar content) were greater than 0.5. Three correlation coefficients (softwood in the pulp correlated with temperature and softwood and hardwood sugar content correlated with temperature) which were less than 0.5 were also included for reference. This model was again refined until no correlation coefficients were greater than 0.5. The result of the refinement is shown in Figure 8.

Figure 8 shows the result of using temperature, total reducing sugar content, and lignosulfonate weight fraction in the model. The largest correlation coefficient is 0.20. It occurs between the reducing sugar content and temperature. The smallest correlation coefficient is 0.06 which occurs between the reducing sugar content and the lignosulfonate weight fraction. Thus, the independent variables were determined to be the temperature, the reducing sugar content, and the lignosulfonate weight fraction. After After this analysis these three variables were input into the program SOLVLNL sequentially to determine the coefficients for the gel reaction.

Minimizing the Model Error

SOLVLNL used the linearized form of an Arrhenius type equation so that ordinary linear regression analysis could be used. The equation was based on the multiplicative power law model.

Using the program SOLVLNL, the modeling was began by using only temperature for a variable. While the majority of the variation of the gel time could be accounted for by the temperature, an error of 51% determined from the standard deviation still remained when the calculated gel times were compared to the experimental gel times.

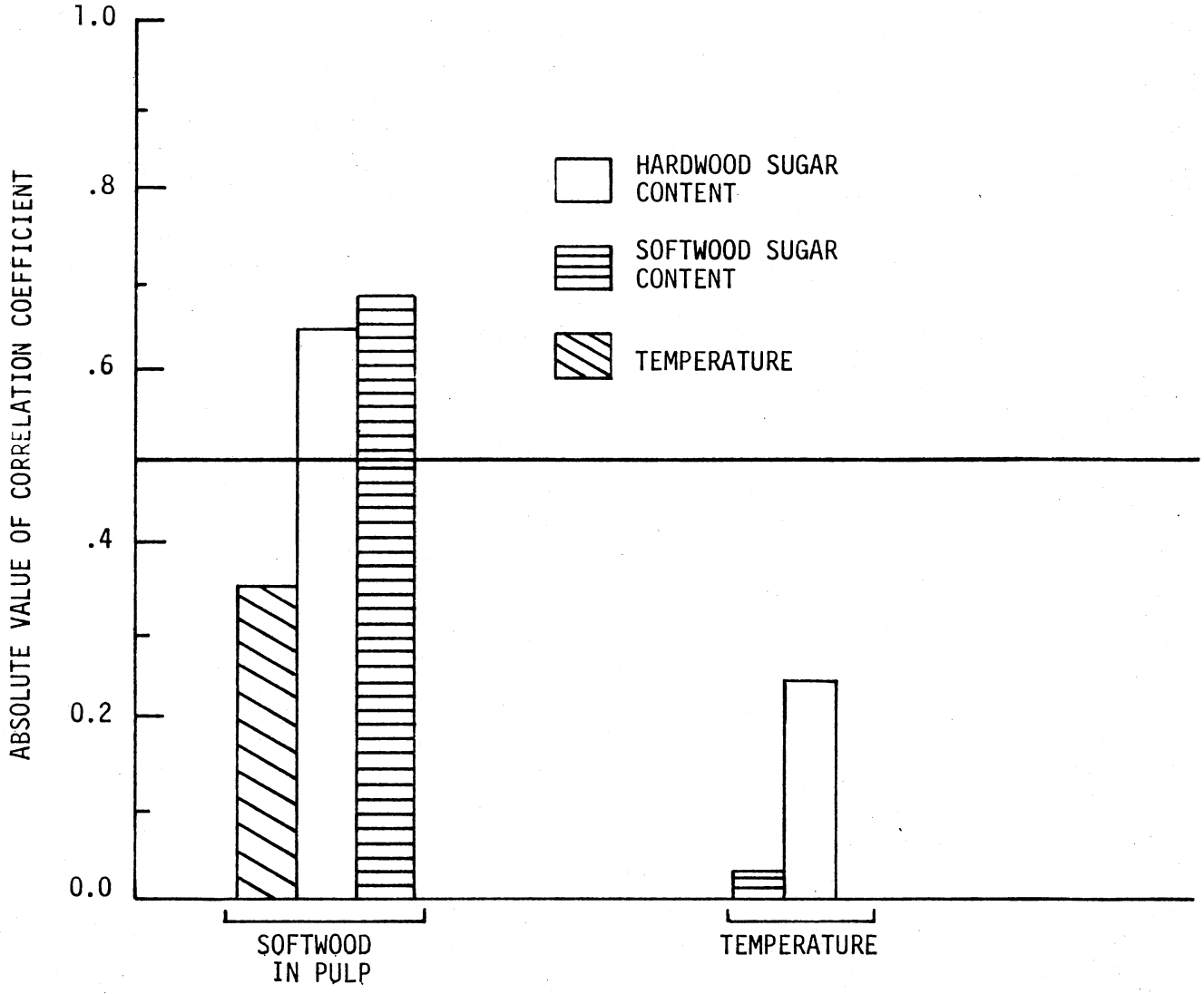


Figure 7. Examples of Correlation Coefficients for Five Variable Kinetic Model

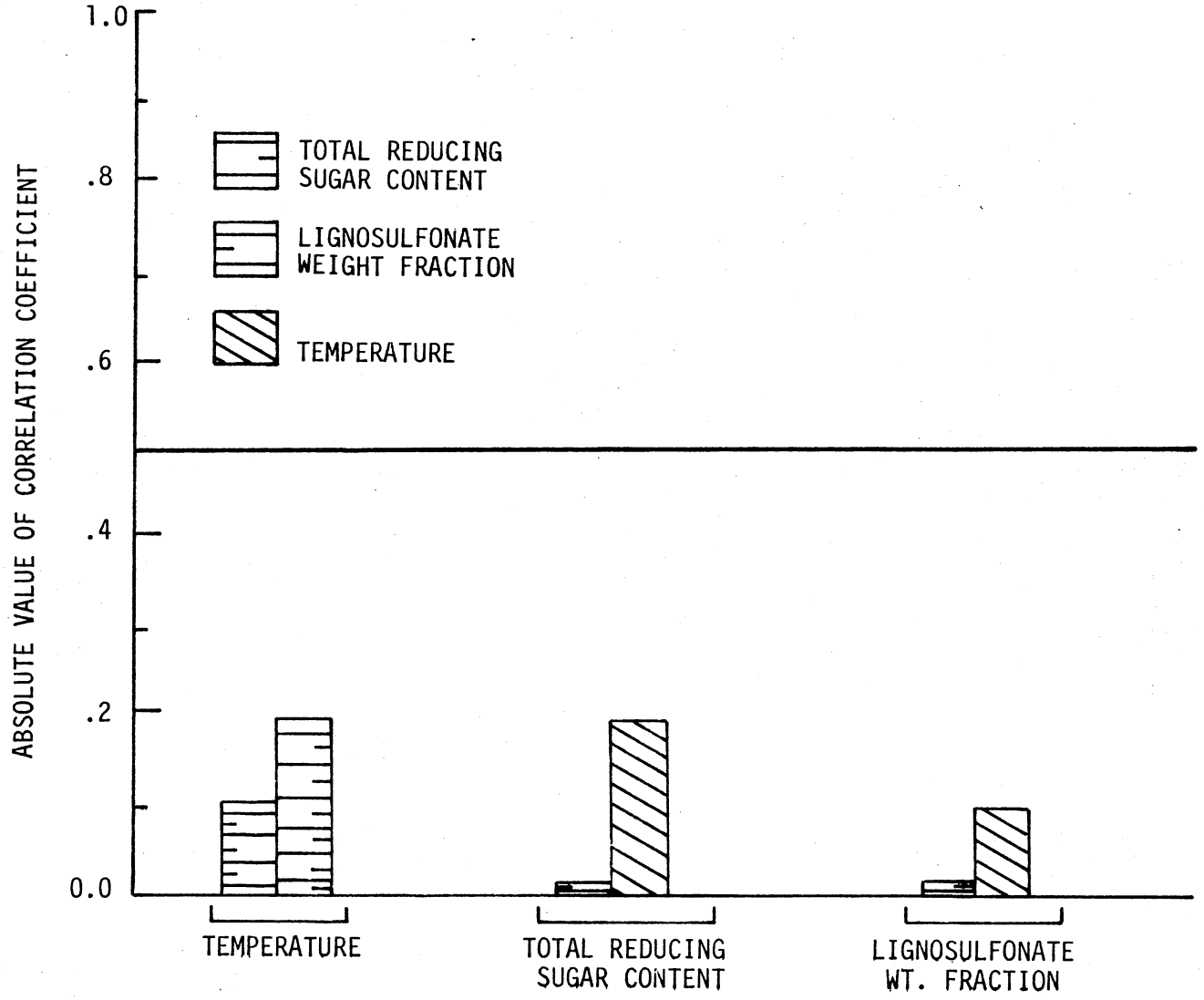


Figure 8. Examples of Correlation Coefficients for Three Variable Kinetic Model

Arbitrarily, the next step was to use temperature and reducing sugar content. This resulted in an error of 31%. The input variables were then changed to temperature and lignosulfonate weight fraction. Using only temperature and lignosulfonate weight fraction as variables, the error for this analysis was 44%.

The final step was to use reducing sugar content and lignosulfonate weight fraction with the temperature in the model. The result of this combination was that the error had been reduced to 23%. This is within acceptable limits as the average error in the gel times taken during this study was 11%; thus, the errors of the model are comparable to the experimental error.

During the model building the coefficients for the input variables varied only slightly as the number of variables were changed. For example, when the reducing sugars and temperature were input, the coefficients determined were −1.1436 and 12306 respectively while when reducing sugars, lignosulfonate and temperature were input the reducing sugar coefficient was −1.1037 and the temperature coefficient was 12526. In this analysis the reducing sugar and temperature coefficients varied 3.5 and 1.8 percent respectively which is well within the experimental error of this work. This small variation of the estimates of the exponents whether the other variables are used or not means that the reducing sugars, the lignosulfonate, and the temperature are essentially independent. This is the definition of variable independence. The model building steps are summarized in Table VI. This analysis shows that the important variables were - in decreasing order - the temperature, the reducing sugar content, and the lignosulfonate weight fraction.

Interpretation of the Model Study

The model which best fits the data is given by

$$\ln \text{Gel Time} = a\ln A + b\ln B + c/\text{Temperature} + D \qquad (5.1)$$

where A is the reducing sugar content, B is the weight ratio of lignosulfonate, D is the

TABLE VI

SUMMARY OF MODEL BUILDING STEPS

Variables	Coeff. Red. Sugar	Coeff. Ligno.	Coeff. Temp.	Const-ant	Standard Devia-tion	Error (%)*
Temperature			11574.	-21.189	.41005	51
Temperature, Reducing Sugar	-1.1436		12306.	-24.897	.26636	31
Temperature, Lignosulfonate Weight Fraction		-.66351	11849.	-23.563	.36743	44
Temperature, Reducing Sugar, Ligno. Weight Fraction	-1.1037	-.59365	12526.	-26.889	.20789	23

* Equals 1 standard deviation from least squares analysis

natural logarithm of the proportionality constant, and a,b, and c are coefficients.

The coefficients and proportionality constant determined from SOLVLNL are as follows:

$$a = -1.10; \quad b = -0.59; \quad c = 12526.; \quad D = -26.89$$

where a and b are essentially the reaction orders for the reducing sugars and the lignosulfonate, c is the activation energy divided by the universal gas constant, and D is the natural logarithm of a proportionality constant relating the rate of the reaction to the gel time. The significance of these constants will be discussed later in this chapter.

These values are valid only if 1) the reducing sugar content is input as fractions (such as .199) not percentages, 2) the lignosulfonate is input as weight fraction such as 0.06, and 3) the temperature is input as degrees Celsius then converted to degrees

Kelvin in the program. The SAS programs were used to generate the plots from the results of the SOLVLNL analysis.

Figure 9 is a plot of the logarithm of the gel time versus the softwood content in the original pulp. It shows the range of gel times observed for each of the three pulp mixes used in this study. For example, at a softwood fraction of 0.66, the gel times vary from a natural log of 3.0(20 hrs.) to 6.4(602 hrs.). This variance in gel times is a result of conducting the experiments at different temperatures. The four distinct groups of data represent gel times taken at 191, 177, 163, and 149^0 (from bottom to top on the plot). The same types of groupings also occur at softwood fractions of 0.97 and 1.00. This presentation of the data shows that the softwood content is not correlated with gel time, i.e., no straight line representing a 1:1 correlation is discernible.

Figure 10 is a plot of the natural logarithm of the gel time versus the reducing sugar content in the lignosulfonates. It shows that four reducing sugars fractions were present in the lignosulfonates used in this work. Thus, the reducing sugar content can vary from manufacturer to manufacturer even though the original pulp mix is the same. For example, for a reducing sugar content of 0.199, the natural logs of the gel times vary from 1.2 (3.3 hrs.) to 6.5 (665 hrs.) as a result of changing the temperature at which the experiments were conducted. The four groups of data represent the four temperatures that this lignosulfonate was studied. This figure also shows that no correlation exists between the reducing sugar content in the original pulp and the gel times.

Figure 11 plots the estimated gel time versus the observed gel time based on the Arrenhius type model described previously. This plot shows a 1:1 correlation between the calculated and observed gel times. This means that the model chosen adequately describes the lignosulfonate gel reaction.

Reaction Orders

The Arrhenius model was used to determine the reaction orders by subtracting the

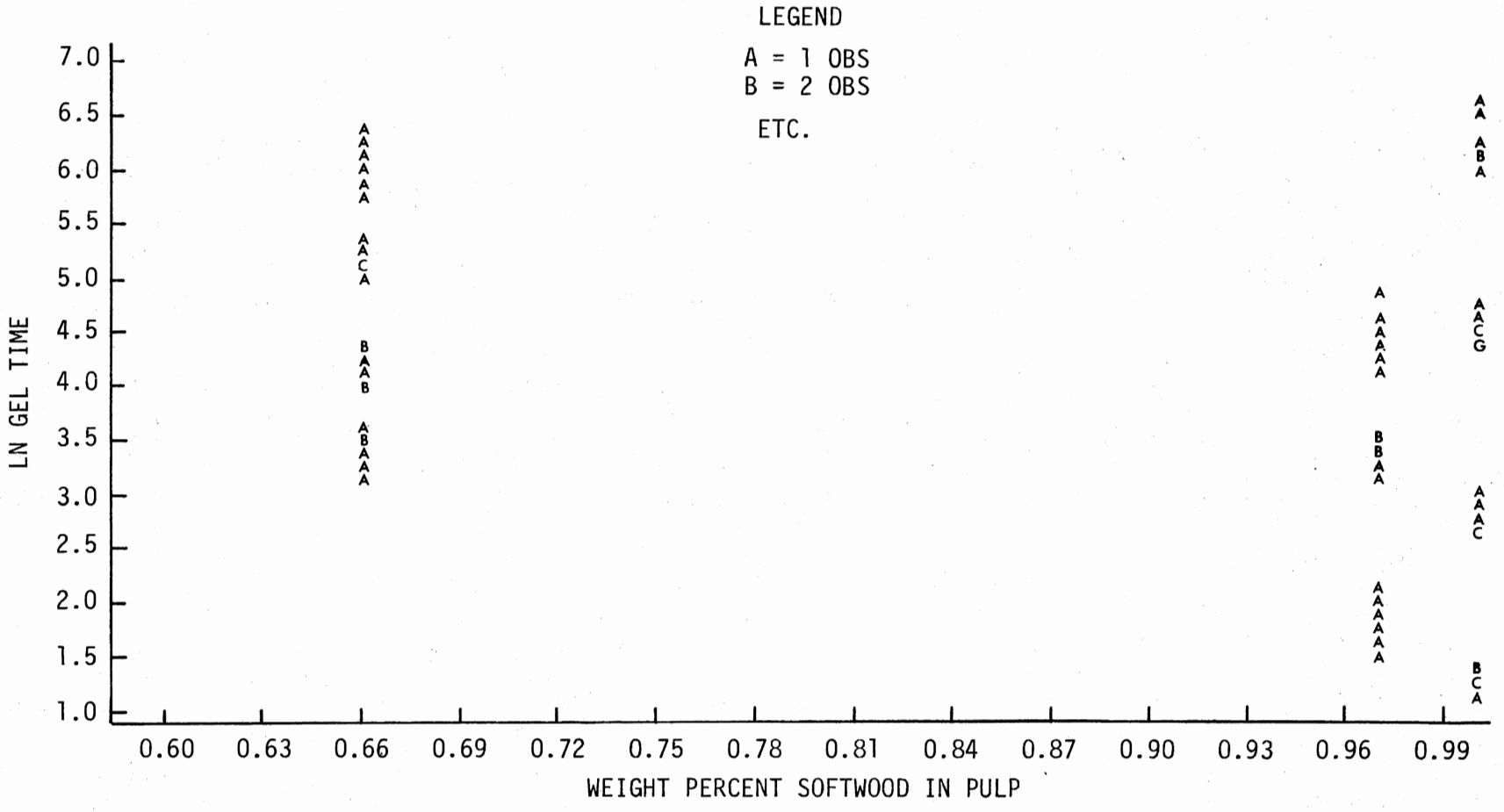


Figure 9. Natural Logarithm of the Gel Time Vs. Softwood Content in the Original Pulp

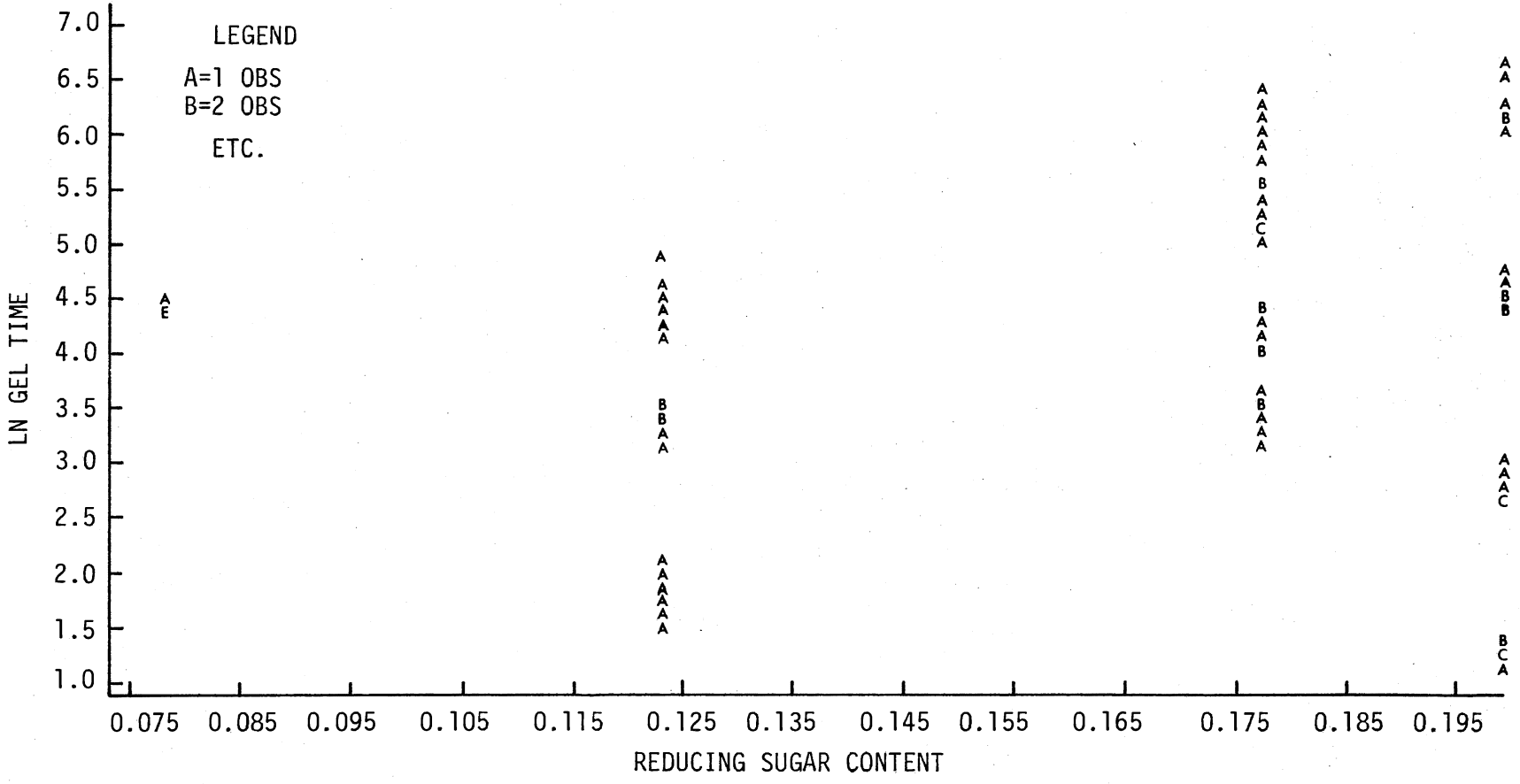


Figure 10. Natural Logarithm of the Gel Time Vs. Reducing Sugar Content in the Lignosulfonates

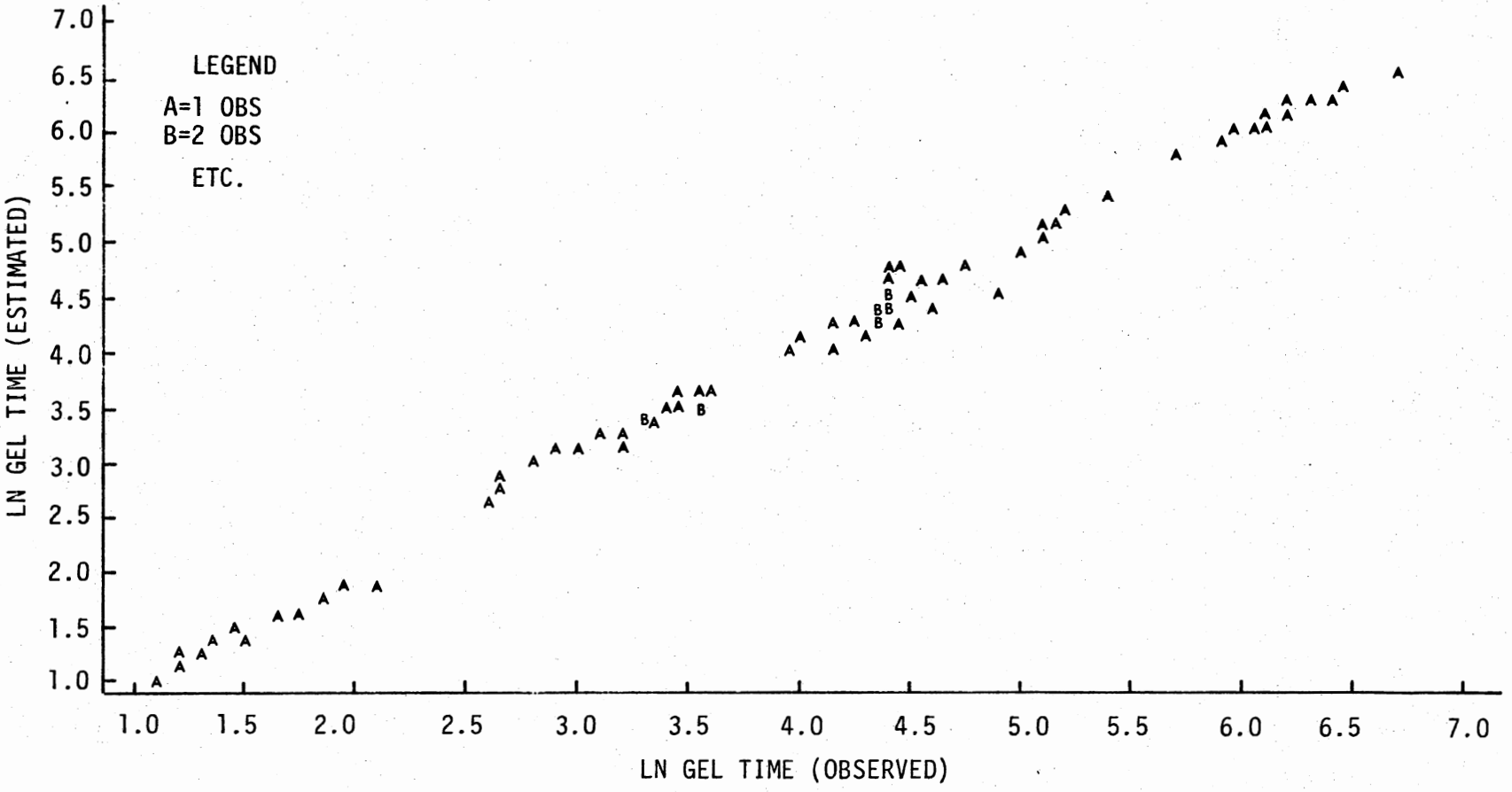


Figure 11. Comparison of Observed Gel Time Vs. Calculated Gel Time From the Model

temperature effects of the reaction. A plot of the natural logarithm of gel time minus the temperature effects versus the natural log of the reducing sugars was generated. This treatment removes the effect of temperature from the gel time data. The curve, which is essentially a straight line, resulting from this treatment allows one to calculate the reaction order for the reducing sugars. On Figure 12 the slope of the line is −1; thus the reaction order for the reducing sugars is one because the gel time is proportional to 1/rate. The small data scatter means that the influence of the reducing sugars on the gel times is large compared to the other components. From this section of the study, a possible explanation of why the gel times recorded for Raylig may be longer than the corresponding gel times for LTA is proposed. The longer gel times may be because Raylig has considerably less reducing sugar than either LTA. Reference Figures 3, 4, and 5.

The data treatment described above is possible because the variables were found to be independent from each other as determined during the model building steps (See Table VI). The variable independence is also demonstrated on Figure 8 where the largest correlation coefficient is 0.20.

When the F-distribution test was run on the reducing sugar content, the results indicated that the sugars had a large effect on the gel times. This test confirms the results observed on Figure 12. The F-test results were that the F-value was 148.42 and the significance probability was 0.0001. This means that the variance associated with the reducing sugars are of a different population than the other variables. By looking the F-value up in a standard statistics table, a 99.9% confidence level can be assigned to this data interpretation because of the number of variables and the number of observations.[52] This is a greater confidence level than is required to establish independence.

Kobayashi[59] has studied the rate of decomposition of the reducing sugars glucose, galactose, mannose, and xylose by sulfuric acid. This decomposition reaction was found to be first order at temperatures below 150°. Although Kobayashi's work was conducted

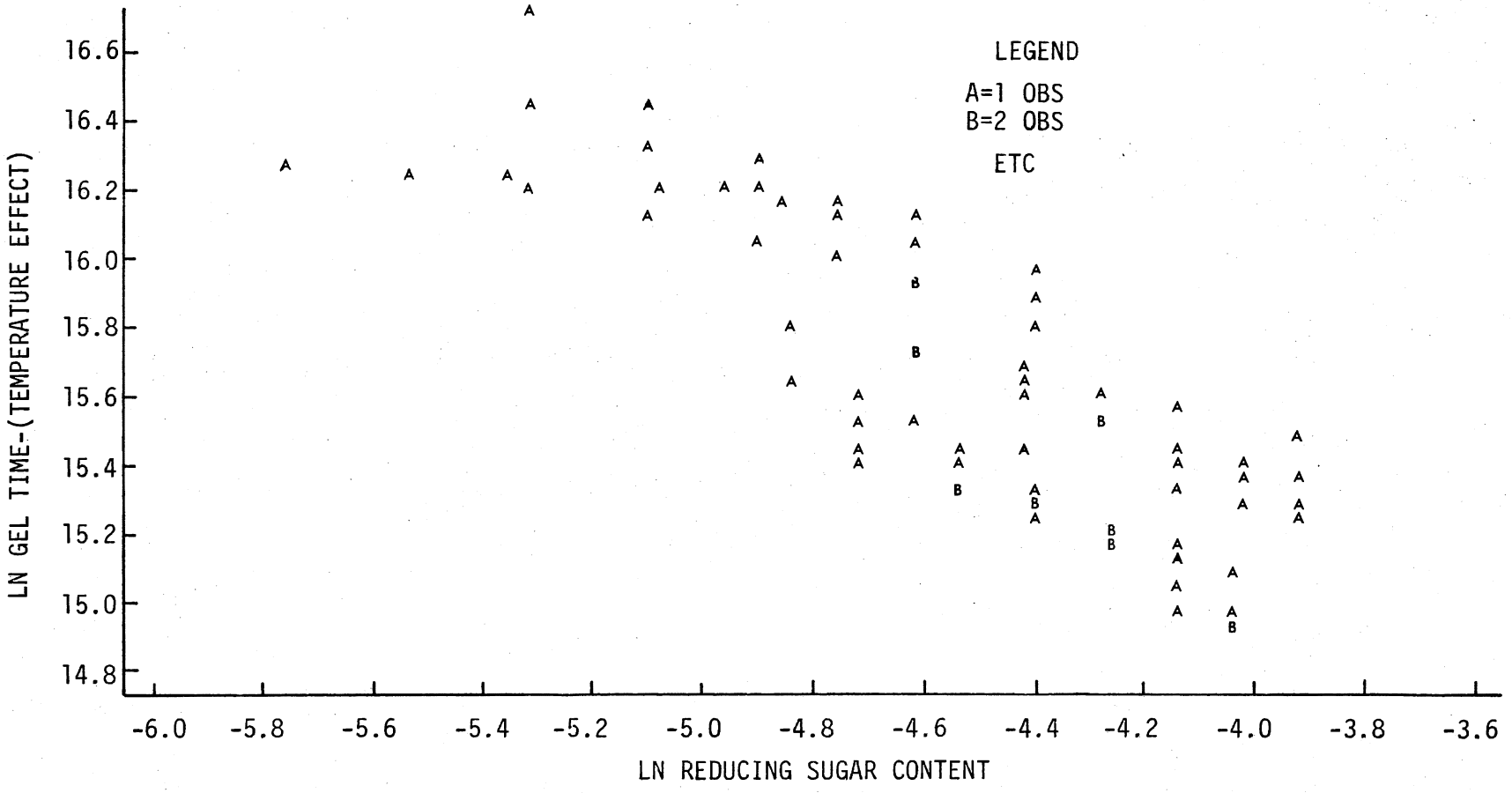


Figure 12. Estimation of Reducing Sugar Reaction Order

at lower temperatures, with pure reducing sugars, and under acidic conditions, it may serve to help explain the chemistry of the reactions reported here. Similarities are that the lignosulfonates contain reducing sugars, and the particular lignosulfonates studied were acidic though the lignosulfonate liquors have other compounds in addition and the reaction temperatures are higher.

By subtracting the temperature and reducing sugar effects from the gel times, the effect of and the reaction order for the lignosulfonates can be determined. Figure 13 is a plot of this effect. The wide band of data on the plot shows that the lignosulfonate content has much less influence on the gel time than the reducing sugars discussed above. This influence could also be decreased because of the other components in the solution which could be interfering with the lignosulfonate reaction but which could not be determined independently from the available data. These 'lurking' variables could be the sulfur content or the effects of other variables that can't be estimated. Even so the slope of the line should equal the lignosulfonate reaction order. Using a purchased mathematical package, a least squares fit of the data calculated the slope to be -0.66. This compares with the coefficient (-0.59) determined for the lignosulfonate weight fraction during the model building portion of this work. The differences between these two least squares results could be the result of different matrix inversion techniques or in round-off error. The slopes are negative because the gel time is inversely proportional to the rate.

The calculated reaction order compares favorably with the number of sulfur groups that can be attached to the lignin backbone. Figure 14 shows the nine possible sites for the sulfur to react during the pulping process. Each reaction site is enclosed in a circle. However, only 1 out of 2 or 1 out of 3 sites do react.[60] Because it would be difficult to determine the amount of sulfur attached to the lignosulfonate backbone, the more convenient term - the lignosulfonate weight fraction - was used in the model. As a result, the reduced reaction order may reflect the active sulfur in these lignosulfonates. If the

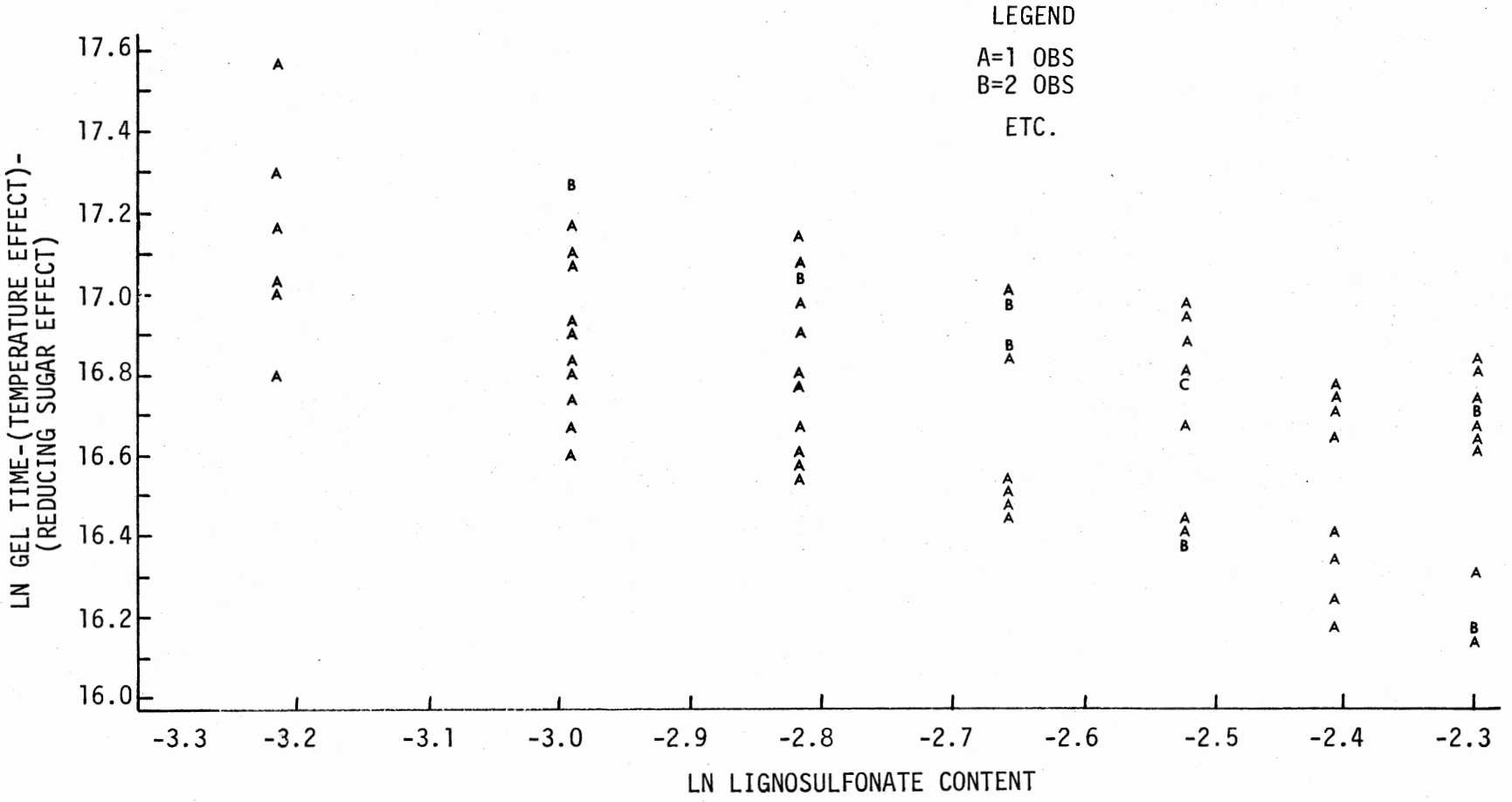


Figure 13. Estimation of Lignosulfonate Content Reaction Order

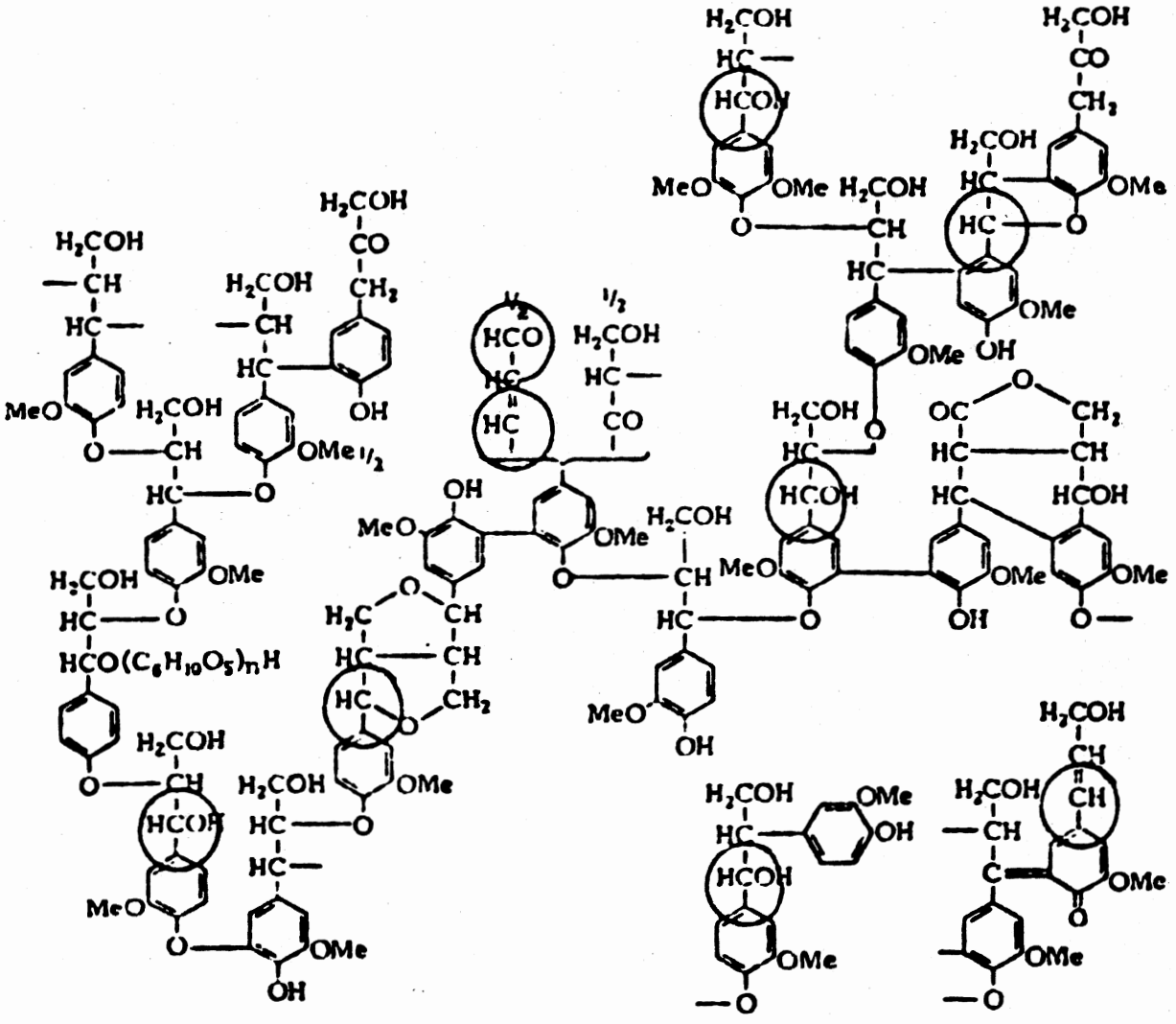


Figure 14. Partial Structure of Lignosulfonate

sulfur were one of the active sites, the derived order for the lignosulfonate weight fraction is in the range possible for sulfur addition to the backbone according the labelled compound studies conducted by other workers in the field.[60]

Variances from a least squares fit of the natural logarithm of gel time minus the temperature and reducing sugars effects versus the lignosulfonate weight fraction were run. The results show that the F-value is 19.68 with a significance probability of 0.0001. This compares with the F-value of 148.42 for the reducing sugars discussed above. Even though the significance probabilities are equivalent, the magnitude of the reducing sugar F-value relative to that of the lignosulfonate weight ratio confirms that the reducing sugars have a greater effect on gel time than the lignosulfonate weight fraction does. This analysis also shows that the variances of the reducing sugars and the lignosulfonate weight fraction are from different populations, therefore they are independent variables.

If additive reactions are occurring, the additive rather then the multiplicative model should be used to describe the reaction. But if additive reactions were occurring and this were not recognized, the analysis presented here, i.e., the multiplied model, would be most correct if the reducing sugars gel much more quickly then the lignosulfonates. If the reducing sugars do control the reaction, the estimate of the reducing sugar reaction order may be more accurate. A corresponding reduction in the accuracy of the reaction order estimate for the lignosulfonate weight fraction may occur. Both of these estimates may be biased as a result of using an incorrect model to describe the reaction.

Activation Energy and Possible Mechanisms

In general, to determine an activation energy, rate constants are determined at several temperatures. If the Arrhenius relationship is applicable, a straight line will be obtained when plotting ln k (the rate constant) versus 1/T. The activation energy can be determined from the slope of this line. The frequency factor A is the intercept.

However, this treatment is valid only if the same reaction occurs at all the temperatures studied and only if the temperature range studied is large i.e., a temperature range of only 11^0 is inadequate.[61]

During this study, the rate constants were never determined. This is in contrast to the usual method used for determining activation energies. Although the treatment used for determining activation energies is unusual, it is not unique.

Sethi and Devaprabhakara[62] estimated the activation energy of the pyrolysis reaction of *endo*-dicyclopentadiene without first determining the rate constants at several temperatures. Their value, 33.01 kcal, agreed within 2% of the previously published value of 33.70 kcal.

Schmiegel et al.[63] determined activation energies of compounds such as *cis*-stilbene and norbornene without determining the rate constants. The activation energy for *cis*-stilbene determined by Schmiegel et al. was 42.6 kcal/mol. The previously published literature value was 42.8 kcal/mol. Similarly, for norbornene the previously reported value was 42.8 kcal/mol while the Schmiegal et al. value was 41.3 kcal/mol.

In work by Lindstrom[64] a Kraft Black Liquor gelation reaction study was conducted. Kraft Black Liquor is a co-product from the Kraft pulping process of paper just as lignosulfonate is a co-product from the sulfite pulping process of paper. In the Kraft Black Liquor study, the gel times were the basis of the analysis. However, the temperature range used in the Kraft Black Liquor work was from 25 to 69^0. Even so, this is analogous to using the lignosulfonate gel times as the basis for a study such as that reported here. For this Kraft Black Liquor work the rate constant variation with temperature was not determined, but an activation energy of 38,300 cal. was calculated.

In this study the temperature ranged from 149 to 232^0. According to Krug et al.,[61] this temperature range is large enough for the Arrhenius relationship to be applicable if a straight line is obtained when plotting the natural logarithm of the gel time versus 1000/temperature. Figure 15 shows that a linear relationship does exist when the

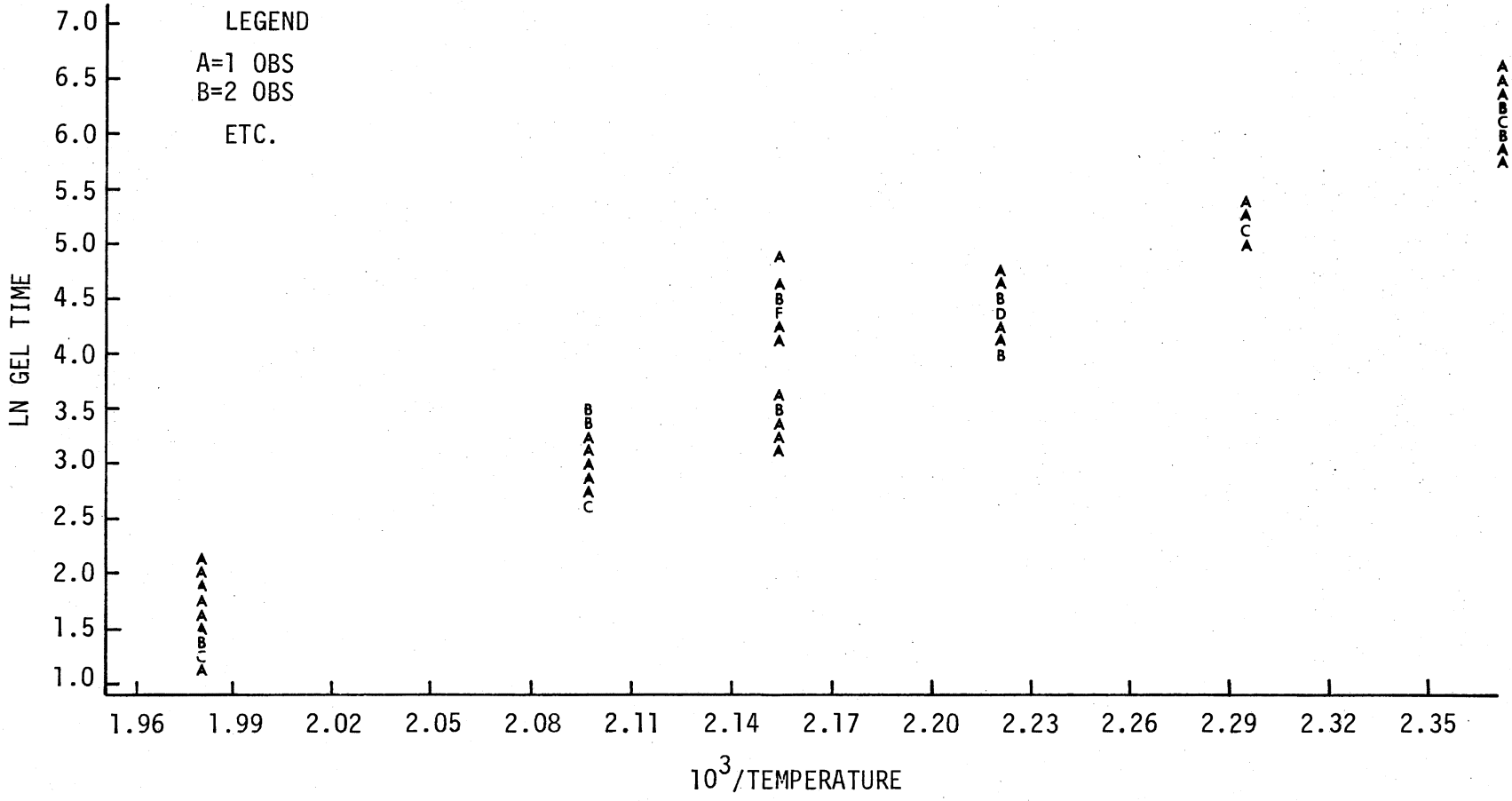


Figure 15. Estimation of Activation Energy for Lignosulfonate Gelling Reaction

natural logarithm of the gel time is plotted vs. 1000/temperature. The slope was used to estimate the activation energy for the high temperature gelation of lignosulfonate. An activation energy of 26,000 cal was calculated from the slope on Figure 15. The data scatter on Figure 15 is less than that on Figures 12 or 13. Therefore, the temperature influences gel time more than any component in the lignosulfonate.

Figure 16 is a plot of the natural logarithm of the gel times which have had the influences of the reducing sugar and lignosulfonate subtracted from them versus 1000/temperature. This figure confirms that the activation energies are approximately equal at all the temperatures studied because no curvature is obtained when these two variables are plotted against each other. The data scatter has been further reduced. Comparison of the data scatter at 2.15 on Figure 15 with that at 2.15 on Figure 14 shows that for Figure 15 the change across this band is 1.25 while Figure 14 has a change across it of 1.75. The difference (0.5) is the contribution of the reducing sugars and the lignosulfonate content to the gelling reaction.

Handy et al.[65] have done a study on surfactants which contain sulfonates. The purpose of this work was to determine the activation energy of decomposition at high temperatures. In their work the activation energy calculated was 25,400 cal. It could be that the sulfonate groups in the lignosulfonates are undergoing an analogous reaction to the petroleum sulfonates since the calculated activation energies are nearly equal. However, if this were to occur, it would mean that the reducing sugars and the lignosulfonates are undergoing decomposition independently. This seems to be contradictory to the analysis of the results of this study because the multiplicative rather than the additive the power law model describes the lignosulfonate system.

Another possibile mechanism for the lignosulfonate gel reaction could be the formation of ketenes from the carbohydrate pyrolysis intermediate - glycolaldehyde. Kang et al.[66] studied the pyrolysis reactions of sugars such as glucose, galactose, and mannose. They found nearly quantitative yields of ketene and water which suggested that the sim-

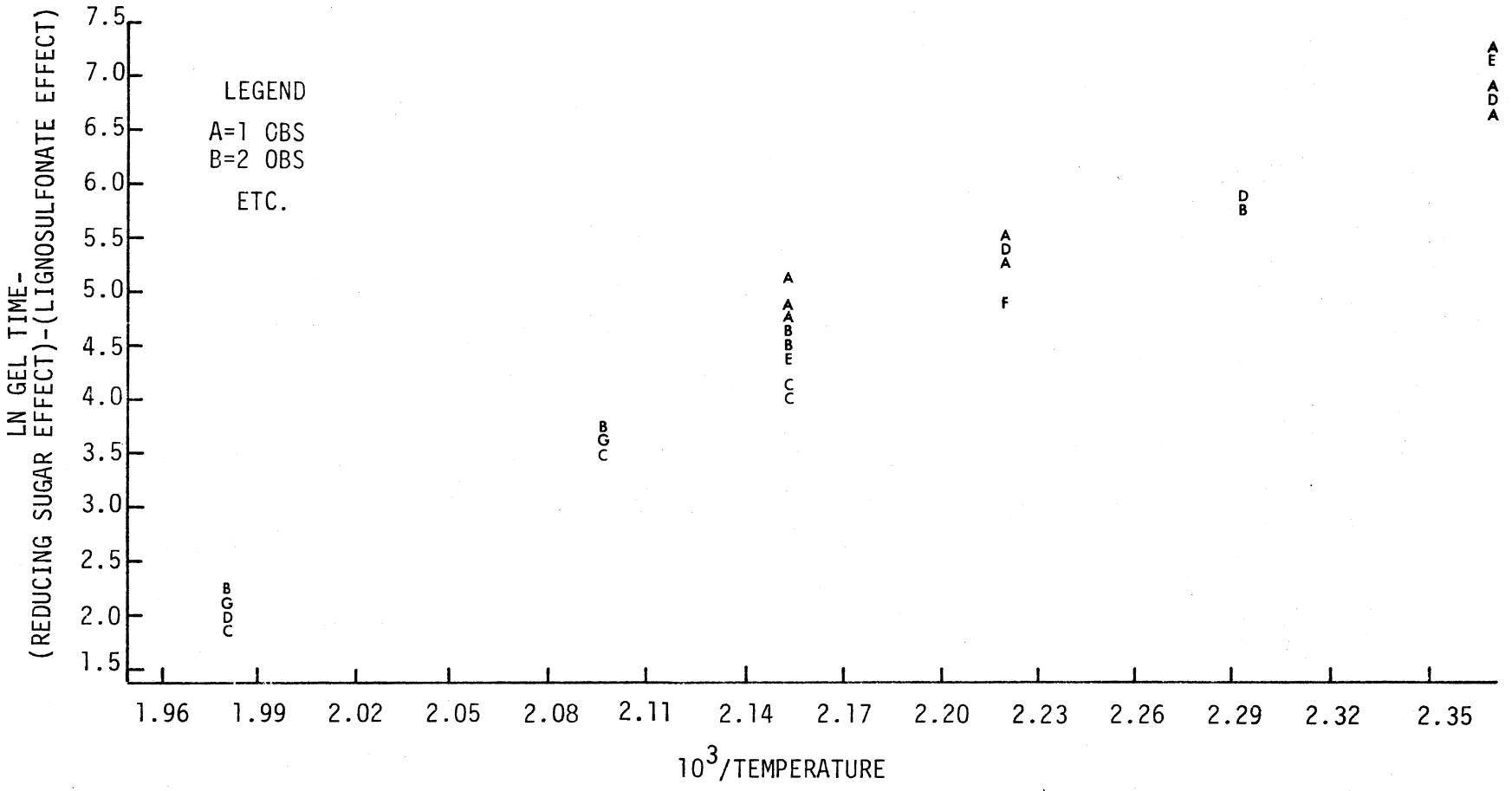


Figure 16. Confirmation That Similar Reactions Are Occurring at All Temperatures Studied

ple dehydration of the glycolaldehyde intermediate was occurring at temperatures as low as 200°. No rate data was given in their work.

The reaction orders (1 and 0.59) determined during the model building section of this study are consistent with the known structure of lignin. See Figure 14. A possible gelling mechanism could be a redox reaction between the reducing sugars and the sulfonate groups on the lignin backbone.

To prove which hypothesis is correct, i.e., redox, decomposition, dehydration, or combinations of all three, work would have to be done with pure compounds under the conditions used here.

Summary of Results of Lignosulfonate Study

This study has shown that dilute lignosulfonate solutions can gel at temperatures above about 149°. In the lignosulfonate system, the viscosity increases until a stiff gel is produced. All gels above 5 weight percent lignosulfonate concentration have viscosities greater than about 3,333,000 cp.[28] The lignosulfonates studied have gel times that are on the order of hours (e.g., 2 hours to 33 days instead of minutes) which can be attained at temperatures up to 232°.[28] The gel time is controlled principally by temperature; the higher the temperature, the shorter the gel time. Gel times are also affected by reducing sugar concentration and, to a lesser degree, the lignosulfonate content. Lignosulfonate concentration affects the gel time even less than the reducing sugars.

This study has demonstrated that gel time data, analyzing all temperatures as an entity and treated statistically, can be used to determine the factors which affect the gelling reaction. It is also possible to determine the reaction orders for the reducing sugars and the lignosulfonate. The data can be used to calculate the activation energy for the gelation reaction.

The results of the kinetic study are 1) the important variables are - in descending or-

der - temperature, reducing sugars, and lignosulfonate content; 2) the gel time data of the natural polymer lignosulfonate can be used to determine kinetics of the system; 3) the reaction orders are first order with respect to reducing sugars and 0.6 with respect to lignosulfonate; 4) the reaction could be one of three with the most likely being a redox reaction with the reducing sugars reducing the sulfonate on the lignosulfonate backbone; 5) the activation energy for this reaction is 26,000 calories; 6) the variables are not highly correlated and the temperature effects are linear which allows one to analyze the variables together or independently (This data treatment may not necessarily be valid for other systems); and 7) the model proposed provides a basis for predicting the gel times (within ± 23%) as a function of temperature, reducing sugar content in the original pulp, and lignosulfonate weight fraction for the lignosulfonate liquors tested and possibly for new, commercial lignosulfonate products.

CHAPTER VI

RECOMMENDATIONS FOR FURTHER LIGNOSULFONATE INVESTIGATIONS

To better understand the lignosulfonate liquors, two approaches can be used for further study of the gelation reaction.

The first approach could be to add reducing sugars to the commercial products. Mannose would be a likely sugar to start with because it is most prevalent in the raw lignosulfonates. Combinations of the other reducing sugars such glucose and galactose could also be added to the lignosulfonate for study. The purpose of this study would be to identify which sugar most affects the gelling reaction.

Another set of experiments could be the fractionation of the lignosulfonates. This separation work would be analogous to the *d-l*, *meso* separation of 2,3-dimethyl succinic acid reported by Purdie et al.[67] The fractionation process would decrease the amounts of reducing sugars present. The purpose of this work would be to determine the minimum requirement of reducing sugars for the reaction to occur. For example, ITT Rayonier has studied lignosulfonates which were free of reducing sugars; in this work, gels did not form under conditions comparable to those reported here.[68]

CHAPTER VII

INTRODUCTION FOR TRANSITION METAL ETHYLENE-MALEIC ACID STUDY

Before undertaking a discussion of polymers, it is fitting to define the basic terminology. Classically, a polymer or macromolecule is defined as a substance composed of molecules - the composition of which is a multiple of the corresponding monomer or monomers. Another frequently encountered description of a polymer is that of 'a rather large molecule composed of small primary molecules chemically bound together'. Dimers are technically polymer molecules, but a typical polymer is usually assumed to have 20 or more monomer units. A macromolecule is therefore generally a long flexible chainlike structure of appreciable length. In solution it will change configuration continuously under the influence of thermal motion and Brownian movement. With the advent of better technology and improved theory of macromolecules in solution, polymer chemistry has risen from virtual obscurity to assume a large part of the chemical industry. Polymer chemistry was not, however, always considered a branch of chemistry.

Historical

In 1871 Hlasiwetz and Habermann[69] proposed that some naturally occurring substances - e.g., rubber, proteins, and gums - were polymeric in nature. However, at this time acceptable organic research consisted of synthesizing and isolating pure compounds of known molecular weight. Herein lay much of the trouble which led to the early confusion in polymer chemistry. Chemists had believed for years that rubber, and other natural occurring polymers were made from colloidal aggregates of small

molecules held together by some undefined binding force. The belief grew that substances could under proper condition be transformed to colloidal state, and conversely that colloidal substances were physical aggregates of simpler molecules. This belief retarded the developments in the field of polymer chemistry for nearly half a century.

In 1929, W. H. Carothers[70] started a series of investigations in which polymeric molecules were prepared by established organic reactions and the properties of the products were correlated with polymer structure. The first supermolecules synthesized by Carothers had molecular weights on the order of 2500 to 5000. They were waxy materials incapable of being formed into fibers. It was not until he synthesized macromolecular materials with molecular weights greater than 15,000 to 25,000 that distinctly new products were achieved. This work was particularly effective in breaking the last resistance to the new theories. It opened up the field of chemistry to the synthesis of polymers, and established polymer chemistry on a firm chemical footing. Even then the fundamental concept that high polymers are actually high molecular weight compounds with covalent bonds as the force binding atoms together was not generally accepted until after 1930.

Polyelectrolytes

In 1948 Fuoss[71] proposed the suitably fitting name polyelectrolytes for the group of substances which from the molecular point of view were polymers but whose electrochemical and solution properties bring them into the realm of electrolytes. Polymers of this kind differ from non-electrolytes. They are soluble in polar solvents, conduct electricity, and are affected by Coulombic forces between the charges they possess. The configuration of the polyelectrolyte molecule in dilute solution may be greatly expanded by the electrostatic repulsion between its charged groups.

Types of Polyelectrolytes

Much of the early work was carried out on proteins[72] and on synthetic organic ionizable polymers. Polyacrylic acid,[73] polymethacrylic acid,[73] and polyvinylamine[74] are examples of polyelectrolytes studied which have weakly acidic or basic ionizable groups. Strongly acidic and basic polymers such as polyvinylsulfonic acid,[75] polystyrenesulfonic acid,[76] and the quaternized form of polyvinylamine[77] are also known. Polyphosphates[78] and polyisocyanurates[79] are examples of inorganic polyelectrolytes.

An interesting group of polyelectrolytes are copolymers, especially the hydrolyzed copolymers of maleic anhydride. Examples of these compounds are styrene-maleic anhydride[80], vinylethylether-maleic anhydride[80] and ethylene-maleic anhydride.[81] Hydrolysis of these copolymers leads to macromolecules containing spaced pairs of carboxyls. The titration curves of such macroions have lead them to be called 'polydibasic acids'.[82]

Solution Behavior of Polyelectrolytes

For simple electrolytes the binding of a water molecule by an ion will lead to a decrease in entropy, negative ΔS; and this decrease may be expected to be most dramatic with small ions and those of high charge such as an ionized macroion.[83] The structure-breaking effect accompanying ionic solvation will result in a reduction of the number of hydrogen bonds as compared with the number of pur water.[84] Shoolery and Alder[85] concluded that the principal effect of the large univalent electrolytes was to break down the water structure while multivalent ions predominantly polarized the water.

In most cases the study of polyelectrolytes is regarded as an extension of the studies on simple electrolytes. The solution behavior of these electrically charged polymers is largely accounted for by the dominant concept that the electrostatic interactions are bet-

ween ionized groups with the solvent serving as the continuous dielectric medium. Although this picture has provided useful models for the interpretation of typical phenomena, such as counterion binding and many transport properties, it should be considered an oversimplification. In fact, in the rapidly developing field of solution properties of globular proteins, the structure of water surrounding the polyelectrolyte has been recognized as a factor of paramount importance in controlling conformational stability of the molecule.[72,86] If the polyion has a well-defined shape, then the main distinction from simple electrolytes can be considered to be the high charge of the polyion. With flexible chain polyions, the fixed charges may be separated from each other, to some extent, as the chain expands when the system is diluted. Nevertheless, effects produced by the interaction of ionic charges will not vanish in the limit of infinite dilution, as they do in solutions of simple electrolytes.

When a polyelectrolyte is ionized, the interactions between solute and solvent are like those of small ions only a larger contribution to the energy on the solution is made. The electrochemical behavior of polyions in solution also reflects the effect of the macroion on counterion binding,[73] ionic activity coefficient,[87,88] ion-pair formation,[89] ionization equilibrium,[90,91] and conductance.[92] Thus, the problems of electrostatic repulsion of fixed charges and the electrochemistry cannot be strictly separated. It is this interdependence which contributes to the complexities in this field.

As an example, when alkali is added to vinylethylether-maleic anhydride, the coiled molecule begins to expand because of electrostatic repulsion between the charged groups.[80] This has marked effects on the properties, such as viscosity, of the solution. In the absence of added salts the chain of the neutralized acid appears to be almost fully extended which in turn rearranges the water molecules causing ΔH^0 to change. Thus, ΔH^0 and ΔS^0 are of potential value to a better understanding of polyionic processes in solution; and when the role that the solvent plays is better understood, significant new advances in solution chemistry may be reached.

Solution Behavior of Polyelectrolyte-Metal Complexes

The free energy change for the equilibrium process in which a metal ion interacts with a polyelectrolyte has been measured by many methods.[93] The free energy values tend to be large which is indicative of a very stable complex. From free energies alone it is not possible to conclude the nature of the interaction of the intimate structure of the complex. The mechanism for binding may be[94] (1) electrostatic in character and therefore dependent upon the charge of the counterion or (2) site binding and therefore dependent upon complex formation. This distinction is analogous to the one made between ion pairs and complexes for metals with monomeric ligands. In multistep mechanism kinetic studies,[89] it has been suggested that ion pairs and complexes exist in equilibrium with each other and with the free aquated ions. Consequently, both mechanisms may operate, to a greater or lesser extent, depending upon the structure of the polymer and upon the identity of the anionic repeating unit. Preferential site binding can be expected to be significant when the same effect manifests itself in the low molecular weight or monomeric units of the polymer; e.g., in polycarboxylates and polyphosphates[95] as opposed to polysulfonates, which behave as strong acids.[95,96]

Long-range or purely coulombic interaction would be comparable to Bjerrum[97] ion-pairs in simple monomeric systems where ion solvation spheres are inviolate. Alternately, there is some evidence[94] for specific site binding which, by analogy with the monomeric ligand systems, would require substitution into the coordination sphere of the cation and might even involve covalent interaction. In reality, both types probably coexist. The predominance of one form over the other varies from system to system. The relative magnitudes of the Gibbs free energy of complexation ΔG cannot be used to distinguish between the two possibilities. The accompanying ethalpy and entropy changes are better quantities to consider when trying to interpret the changes in the immediate

solute-solvent environment. It is important then to determine the heats of association to help interpret the complexation reaction.

Statement of Transition Metal Ethylene-Maleic Acid Problem

Data on the heats of association for metal-polymer complexes are sparse and as a rule have been obtained from the temperature dependence of the apparent formation constants.[98] In these determinations, no consideration was given to the possible variation in heat capacity of the process or of the possible change in types of complexes formed with changes in temperature. Thus, the resultant heat changes are subject to the limitation that the van't Hoff isochore expression is linear over the entire range. To eliminate this problem a study of some divalent transition metal ethylene-maleic acid complexes was conducted. The heats of formation were measured calorimetrically at 25°. Because the copolymer ethylene-maleic acid (EMA) is structurally related to succinic acid, an advantage of studying the heats of association of the EMA-metal complexes is the extensive information available on succinic acid complexes.[99] As a result, the corresponding metal mono-succinate complexes will be used for comparative purposes in discussing the results.

CHAPTER VIII

THEORY AND BACKGROUND FOR TRANSITION METAL ETHYLENE-MALEIC ACID STUDY

Dibasic Acid General Equations

The equilibrium reactions for a dibasic acid are

$$H_2A + H_2O \rightarrow H_3O^+ + HA^- \quad (8.1)$$

$$HA^- + H_2O \rightarrow H_3O^+ + A^= \quad (8.2)$$

where H_2A represents the unionized acid and HA^- and $A^=$ correspond to the acid at different stages of ionization. The thermodynamic ionization constants (K_i^0) for a dibasic acid are given by

$$K_1^0 = (a_{H^+})(a_{HA^-})/(a_{H_2A}) \quad (8.3)$$

and

$$K_2^0 = (a_{H^+})(a_{A^=})/(a_{HA^-}) \quad (8.4)$$

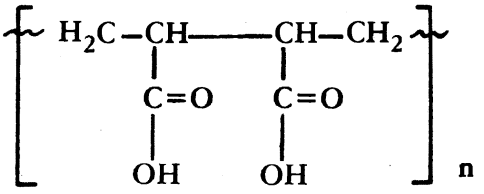
where a is the activity of the various ions and H_2A, HA^-, and $A^=$ are defined above.

The ionization constant of water, the mass balance condition for the total acid concentration, the electroneutrality condition, and the ionic strength equations are used to calculate the respective K_i's for the dibasic acids. The hydrogen ion concentrations are calculated and the activity coefficients can then be determined. The procedure used to calculate the ionization constants is usually a standard iteration around these parameters terminated by convergence on a particular parameter, such as the activity coefficient. After determining the hydrogen ion concentration, the concentration of the other acid species can be determined. The thermodynamic dissociation constants then

can be calculated using concentrations and activity coefficient corrections for acids which have two distinct buffer regions and whose first ionization occurs from a neutral molecule.

Polymeric Dibasic Acid Equations

In contrast to simple dicarboxylic acids, polymeric acid systems



which are treated as dibasic acids cannot be described completely from the equations for simple dibasic acids. For, as pointed out in Chapter VII, the interactions of ionic charges of polyelectrolytes do not vanish at infinite dilution as they do for simple electrolytes; therefore, the possibility of calculating constant K_i's is eliminated. In an attempt to correct for the inability to obtain a constant K_i, several parameters are introduced. One of the parameters which helps to describe a polymer system is the degree of dissociation, α. For a system such as the example given above, α is given by

$$\alpha_1 = (HA^-)/(1 - (HA^-)) \tag{8.5}$$

for the first buffer region and

$$\alpha_2 = (A^=)/(1 - (A^=)) \tag{8.6}$$

for the second buffer region where the concentrations of the polymer ions are given in monomoles/liter. This definition is convenient because each polyacid carries two different classes of carboxyl groups which defines $\alpha = 2$ at complete ionization.

The Henderson-Hasselbalch equation for relating the dissocitation constant, K, to the pH and to α the degree of dissociation is given below.

$$pH = pK + \log(\alpha/(1 - \alpha)) \tag{8.7}$$

If the pH values of simple acids are plotted against $\log(\alpha/(1 - \alpha))$,straight lines with a slope of 1 are obtained. However, it has been observed that the slope for polymeric acids is greater than 1 for the first dissociation of polydibasic acids and for polymethacrylic acid the slope approaches 2.[90] As a result of this variance, Katchalsky[90] introduced the parameter n into the Henderson-Hasselbalch equation. The Katchalsky form is given by

$$pH = pK_i + n \log (\alpha/(1 - \alpha)) - A\mu^{1/2} \tag{8.8}$$

where K_i is the equilibrium constant, i = 1 or 2, A is the Debye-Huckel constant, and μ is the ionic strength.

To determine n for the copolymer under study, one plots pH against $\log (\alpha/(1 - \alpha))$ for both buffer regions. For substituted ethylene-maleic acid copolymers, as a rule n is slightly greater than 1 for the widely spaced first carboxyl groups and is greater than 2 for the ionization of the second carboxyl groups.[80] After determining the value of n for each buffer region, the correction is combined with the appropriate pK to obtain $pK_{i,app}$ - the apparent dissociation constant - which is related to pH by the equations

$$pH = pK_{1,app} + \log (\alpha/(1 - \alpha)) - 0.509\ \mu^{1/2} \tag{8.9}$$

for the first buffer region and

$$pH = pK_{2,app} + \log (\alpha/(1 - \alpha)) - 1.527\ \mu^{1/2} \tag{8.10}$$

for the second buffer region. These two equations were used to determine the transition metal-acid apparent association constants used in the calculation of the heats of formation reported in this study.

Another method of treating polyacids is to make a correction for electrostatic effects. If the polymer is treated as a rodlike model and if it is assumed that the only reason successive ionizations in the polymer differ is a statistical effect, an electrostatic correction is added to Equations 8.9 and 8.10. The general form is

$$pH = pK_{i,app} + \log (\alpha/(1 - \alpha)) + 0.424\ e\ \psi_{el}/kT \tag{8.11}$$

where $e\psi_{el}$ is the electrostatic potential necessary to remove H^+ against the strong forces of the charges already present in the molecule.[100] Since the magnitude of $e\psi_{el}$ should be

dependent on the effects of nearest charged groups, the potentiometric titration curves should reflect the differences in the conformations of the polyions. This effect is caused by the charge separations of the carboxyls which are not far enough apart to be considered non-interacting. Nagasawa and coworkers[101,102] and Gregor and Kagawa[103] have studied this electrostatic influence in atactic, isotatic, and syndiotatic polyacrylic acid and polymethacrylic acid. These authors concluded that to verify unambiguously that the differences observed between the titration curves of the three conformational forms is very difficult. As a result, the differences have been attributed to the flexibility of the polymer chain (i.e., the polymer is not rodlike). It would be desirable then to take into account the flexibility of the polymer backbone in the theory. Until the theory is extended, the application of the rodlike model should be restricted to relatively stiff polyelectrolytes or to data at a high degree of neutralization.

Influence of Counterion Binding and Neutral Salts

While the titration behavior of low molecular weight acids and bases is independent of the nature of the base or acid used as a titrant, this is not the case with polymeric acids and bases. Gregor and Kagawa[103] observed that the titration behavior of polymers was dependent in part on the specific acid or base used. Polyelectrolytes then further complicate the titration curve by binding the counterions of the titrant. This is considered one of the more important characteristics of macroions.[94]

Katchalsky and Spitnik[90] studied the effect of $CaCl_2$ and NaCl on polymethacrylic acid at half-neutralization. The pH decreased in the presence of the salts and continued to decrease with increasing concentration of the salts. This result is indicative of ion binding and demonstrates the futility of titrating polyelectrolytes in the presence of varying concentrations of neutral salts.

Sodium and lithium binding with polyacrylate was studied by Eldridge and

Treloar.[104] They found that cobalt-polyacrylate complexes were in competition with the sodium or lithium to the extent that these two ions were in solution. Lithium was the more efficient in competing with the cobalt for the polyacrylate. This work reinforces the work of Katchalsky and Spitnik discussed above.

Polyionic-Metal Association Constants

All these interactions 1) the degree of ionization, 2) the electrostatic effect, 3) the stereochemical effect, 4) counterion binding, and 5) the salt effect must be considered to gain an appreciation of the difficulties encountered in determining the thermodynamic constants of polyelectrolytes and metal complexes in which the polyelectrolytes participate as ligands. As a result of these interactions, one can only determine the apparent association constants between metal ions and polyions as opposed to determining thermodynamic constants for the monomeric counterparts. Even so, these apparent association constants (K_{assoc}) can then be used to determine other thermodynamic properties such as ΔG^0 since

$$\Delta G^0 = -RT \ln K_{assoc} \tag{8.12}$$

Additionally,

ΔS^0 can be calculated after ΔH^0 has been measured because the Gibbs free energy is related to the enthalpy and entropy by

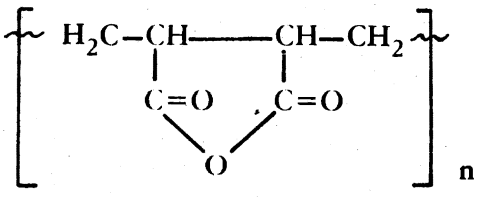
$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{8.13}$$

CHAPTER IX

EXPERIMENTAL FOR TRANSITION METAL ETHYLENE-MALEIC ACID STUDY

Description of the Polymer

The alternating 1:1 copolymer of ethylene and maleic anhydride was synthesized by Hanford[105] in 1945. Machi et al.[81] also synthesized and studied EMA. The infrared spectrum had characteristic peaks which indicated that the copolymer was composed of the methylene group of the ethylene monomer and the cyclic anhydride of the maleic anhydride monomer. See figure below. From the spectrum, Machi and his coworkers determined that the extent of sequence addition was negligible. Later the research personnel of the Monsanto Chemical Company,[106] under the supervision of Johnson,[107] synthesized the copolymer and made derivatives commercially available with molecular weight ranges of 2,000-3,000, 20,000-30,000, and 60,000-70,000. This study involves the 20,000-30,000 derivative which has the structure



where n = 170.

Preparation of Solutions

Deionized Water

The deionized water used in the EMA experiments was prepared by passing distilled water through about three feet of reagent grade Rexyn 300 (H-OH) mixed bed resin (Fisher Scientific Company, Inc.). The water was then passed over a three-foot column of activated charcoal and stored in two 12 liter flasks, which were vented to the atmosphere through Ascarite (8-20 mesh) (Arthur H. Thomas Company) to remove CO_2.

Standard Base

Since competitive ion binding by the cation of an alkali base may occur with polyelectrolytes,[108] tetramethylammonium hydroxide (QOH) was used to avoid this complication. The standard QOH was prepared from a 10 percent by volume stock solution of tetramethylammonium hydroxide supplied by Eastman Organic Chemicals. One hundred ml of the stock QOH was added to 900 ml deionized water which had been swept free of CO_2 and stored under a nitrogen atmosphere for approximately two hours at room temperature prior to the addition of QOH. The resulting solution was standardized potentiometrically against approximately 2.5×10^{-3} moles of dry, chemically pure potassium acid phthalate (Baker) dissolved in deionized H_2O free of CO_2. In all instances the concentration of the base was approximately 0.1M.

Ethylene-Maleic Acid

In order to prepare the acid with a concentration of 0.01M - based on monomer molecular weight - about 0.5 grams of copolymer, EMA, was hydrolyzed to the acid (HEMA). This was done by warming the anhydride in approximately 400 ml of deionized water at 70^0-80^0 for a period of two hours. The solution was cooled, filtered, and made up to one liter. Because bacteria and mold readily consumed the polymer at

room temperature, solutions were stored at 5° in Pyrex containers with a ground glass stopper.

Metal Perchlorates

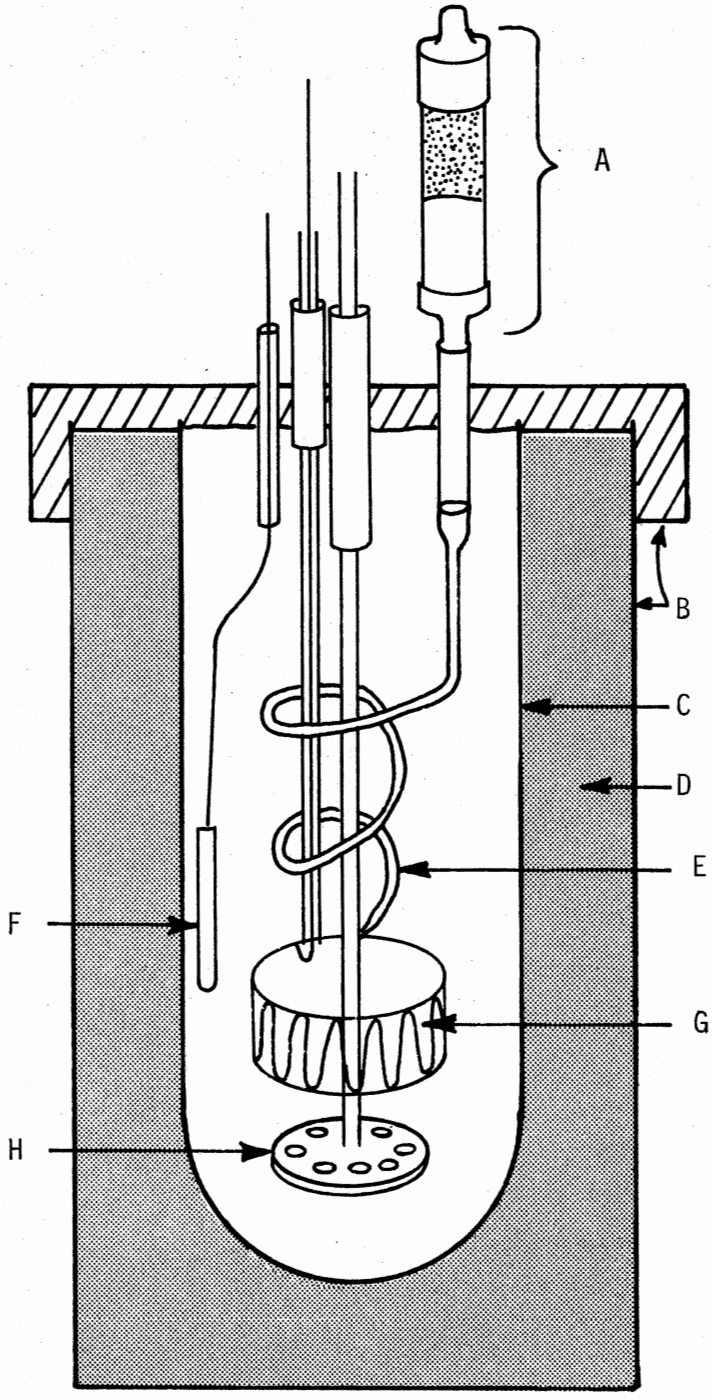
Chemically pure transition metal perchlorates as the hexahydrates were purchased from G. Frederick Smith Chemical Company. The solutions were approximately 0.05M in metal ion. Solutions were stored at room temperature in Pyrex containers with ground glass stoppers. Standardization of the solutions was done by passing a two ml aliquot through a column loaded with acidic Dowex 50-W-X8 20-50 mesh exchange resin. The exchanged acid on the column was then eluted with 100 ml of deionized water. The eluted acid was titrated potentiometrically with standardized QOH.

Apparatus

Microcalorimeters

A dual titration microcalorimeter system (Figure 17) was used to measure the heats of complexation. Insulated Dewar reaction vessels were enclosed in brass thermal jackets fitted with lids. This design allowed for total immersion in water maintained at 25 ± 0.05°. The solutions were stirred by vertical agitation using a single motor (Corning Model LM-2). This arrangement allowed each compartment to serve alternately as a reaction and comparison vessel. Each vessel had a 22-gauge Teflon delivery needle long enough that an adequate volume of titrant could be kept in temperature equilibrium with the contents of the vessel. Each Teflon needle was sealed with silicone grease to avoid the premature mixing of the metal ions with the contents of the microcalorimeters.

A coulometric current source (Sargent Model IV) was used for electrical calibration. The elapsed heating time was measured on the timer incorporated on the instrument. Temperature changes in both reaction vessels were monitored with a matched pair of



A. MICROMETER SYRINGE

B. BRASS JACKET AND TOP

C. SILVERED DEWAR VESSEL

D. STYROFOAM INSULATING MATERIAL

E. TEFLON TUBING

F. THERMISTER

G. PLATINUM HEATER

H. VERTICAL STIRRER

Figure 17. Schematic of Titration Microcalorimeter

2000-ohm thermistors (GB32-PM12, Fenwal Electronics, Inc.) serving as elements of a Wheatstone bridge. The out-of-balance signal was fed to an intermediate dc amplifier (Leeds & Northrup, No. 9634 Null Detector) with the output being displayed on a single pen recorder (Sargent SR).

Procedure

Calibration of Microcalorimeters

Performance of the calorimeters was checked by measuring the heat of protonation of 1.008 x 10^{-2} M tris(hydroxymethyl)aminomethane (THAM, NBS Standard Reference Material No. 724) with 0.5456 M HCl as the titrant. From a series of measurements, the value obtained was 11.39 ± 0.05 kcal/mol at 25°. After correcting for the heat of dilution, the value agreed to within 0.1 percent of the literature value.[109,110]

Heats of Association

The EMA solutions(approximately 10^{-2} M) were about 25 percent neutralized by adding the appropriate volume of 0.1037M QOH. As mentioned earlier, the quaternary ammonium cation was used because its interaction with the polyelectrolyte is much less than that of the alkali metal ions.[111] The partially neutralized EMA was introduced into the dual calorimeters. The Teflon needles were filled with the appropriate metal perchlorate solutions, approximately 0.5M, with precautions taken to avoid premature diffusion into the EMA solution. After assembly, the calorimeters were totally immersed in a water bath at 25°. Thermal equilibrium of the calorimeters was considered established when a near horizontal ($dT/dt=0$) baseline was recorded. Using a microsyringe, the metal perchlorate solution was then titrated (0.200 ml) into one thermostated EMA solution while the other compartment served as a reference vessel. After the reaction was completed in the first microcalorimeter, it was used as the comparison

vessel while the second microcalorimeter became the reaction vessel. pH measurements were made before and after the additions. A glass electrode-calomel electrode assembly calibrated with a standard buffer solution of pH 4.01 on a Beckmann Research pH Meter Model 1019 was used. From the pH measurements the apparent acid ionization and the apparent stability constants were chosen to correspond with the degree of neutralization. After corrections for heats of dilution and protonation were made, the heats of association were calculated.

Heats of Dilution and Protonation

The heats of dilution were measured by titrating the metal ions into a KCl solution of ionic strength similar to the EMA mixture of acid and salt. Corrections were made to the observed heat changes for the heats of dilution of the metal perchlorates. Since the total volume increase during the titration was always less than 0.5 ml, the heat change associated with this dilution of EMA was neglected. Neglecting the dilution of EMA is possible because the final volume of the reaction was 33.36 ml. The heat of protonation of HA^- was determined by titrating the EMA with 0.4884M $HClO_4$.

Heat Capacity Measurements

For each run the average of two heat capacity measurements were made. One heat capacity measurement was made before the metal perchlorate addition and another was made after the perchlorate addition. The heat capacity measurements were made such that the electrical energy input produced a pen deflection which was approximately equal to the deflection observed in the complexation reaction. Since the heat capacity changed only slightly during each run, the two heat capacity measurements were averaged to determine the energy change of the system.

Energy Change Calculations

Energy changes in calories were calculated from

$$Q_E = D \times \bar{h} \tag{9.1}$$

where D is the pen deflection in centimeters during addition of the metal ion to the EMA and $\bar{h}$ is the average heat capacity of the system in cal/cm. When thermal equilibrium of the calorimeter was not ideal; i.e., $dT/dt = 0$, corrections to D were made using the Regnault-Pflaunder method.[112] The experimental energy change is given by the expression

$$Q_E = Q_{MA} + Q_{H_2A} + Q_{HA^-} + Q_{DIL} + Q_{H_2O} \tag{9.2}$$

where $Q_{MA} = \Delta[MA] \times \Delta H_{MA}$, i.e., the change in the 1:1 metal-acid complex concentration times the change in the heat of formation of the complex; $Q_{H_2A} = \Delta[H_2A] \times \Delta H_{H_2A}$ is the change in the initial EMA concentration times the change in the heat of formation of the acid; $Q_{HA^-} = \Delta[HA^-] \times \Delta H_{HA^-}$ is the change in the partially ionized acid times the heat of dissociation of the acid; Q_{DIL} is equal to the energy change for dilution of the titrant and Q_{H_2O} is equal to the energy change for neutralization. Under the conditions of these experiments Q_{HA^-} and Q_{H_2O} were negligible. By substituting each of these expressions into equation 9.2 and solving for ΔH_{MA}, the heat of formation can be calculated. The equation is given below.

$$\Delta H_{MA} = Q_E - (\Delta[H_2A] * \Delta H_{H_2A}) - (\Delta[HA^-] * \Delta H_{HA^-}) - Q_{DIL}/\Delta[MA] \tag{9.3}$$

CHAPTER X

EXPERIMENTAL RESULTS AND DISCUSSION FOR TRANSITION METAL ETHYLENE-MALEIC ACID STUDY

Acid Dissociation Constants

It has been shown[111] that a simple 1:1 metal to ligand complex was formed according to

$$M^{2+} + A^{2-} \rightarrow MA \qquad (10.1)$$

where M^{2+} is the divalent transition metal, A^{2-} is the ionized EMA, and MA is the complex. In the metal-EMA complexation analysis, the concentration of the polyion (EMA) was expressed in mol/l of monomer.[111] (One monomole consists of one residue of maleic acid and one of ethylene for EMA). Concentrations of species needed in the determination of the heat of this reaction were calculated from the known acid apparent ionization constants ($K_{1,app}$ and $K_{2,app}$), the metal complex stability constants (K_{MA}), the measured solution pH, and analytically determined concentrations of metal (m), EMA (a), and base (b). The following equations were used to describe the system:

$$K_{1,app} = [H^+][HA^-](f_1^2/[H_2A]) \qquad (10.2)$$

$$K_{2,app} = [H^+][A^{2-}](f_2/HA^-) \qquad (10.3)$$

where H^+, HA^-, A^{2-}, and H_2A correspond to the monomeric residues at different stages of ionization and f_i is the activity coefficient and

$$K_{MA} = [MA]/[M^{2+}][A^{2-}]f_2^2 \qquad (10.4)$$

where MA, M^{2+}, A^{2-}, and f_2 were previously defined.

The mass balance equations are

$$m = [M^{2+}] + [MA] \tag{10.5}$$

$$a = [H_2A] + [HA^-] + [A^{2-}] + [MA] \tag{10.6}$$

$$b + [H^+] + 2[M^{2+}] = [HA^-] + 2[A^{2-}] + 2m \tag{10.7}$$

where the above defined terms apply.

Activity coefficients were calculated using the Davies equation[113]

$$-\log f_i = 0.509\, z_i^2\, I^{1/2} / 1 + I^{1/2} - 0.3I \tag{10.8}$$

where

$$I = b + [H^+] + 3[M^{2+}] + [A^{2-}] \tag{10.9}$$

and b, H^+, M^{2+}, and A^{2-} have been previously defined. A computer program[114] solved for the ion concentrations by repetitive iteration to a constant f_1 around equations 10.5, 10.6, 10.7, 10.8, and 10.9. By selecting the apparent ionization constant to correspond with the degree of ionization of the partially neutralized acid solution in the calorimeter vessel, a correction was made for the 'polyionic work' term. In spite of the limitations to this approach, the method was considered to be preferable to measurements in a constant ionic strength medium where uncertainties would have been introduced from competitive binding by the cation of the added salt.

There are two other justifications for calculating activity coefficients for this work. The first is that Haymann[100] has shown that the limiting case which adequately describes the polyionic work (Equation 8.11) exists if the analytical concentration of the polymer is $\leq 10^{-2}$M. This constraint is applicable for this study. The second is that Morawetz[93] has proposed that the concept of ionic strength has meaning in polymer solutions only if the polyionic work is less than kT. The maximum value calculated in this study is 0.7 kT, thus lending credence to the use of the interionic-attraction theory to calculate the activity coefficients.

Heats of Formation

The interaction of polyelectrolytes with their counterions is particularly interesting, since polymers constitute a unique type of chelating agent - intermediate between monomeric ligands and ion-exchange resins. The counterions studied were the divalent ions of the transition metals manganese, cobalt, nickel, copper, and zinc.

The values given in Table VII correspond to the changes in concentration which occur as a result of complexation during the calorimetric runs. The transition metal-EMA formation constants are also listed. These constants vary from a low of 3.76×10^{8} to a high of 4.45×10^{10} for nickel and copper respectively. Other ions reported in Table VII are manganese, cobalt, zinc. The first and second dissociation constants are also included. The values for the dissociation constants for EMA are 1.32×10^{-5} for the first dissociation constant and 2.87×10^{-10} for the second dissociation constant. For more details on the acid dissociation constant and the transition metal formation constant determination refer to Felber et al.[108]

From three experiments in which $HClO_4$ was added to a partially ionized EMA solution, a value of $\Delta H_{H_2A} = -0.24$ kcal/mol was obtained (Table VIII). This is in good agreement with the heats of protonation of similar monomeric dicarboxylic acids.[115] For example, the calorimetric determination of the heats of protonation for the first ionization steps of adipic and suberic acid are -0.30 kcal/mol and -0.34 kcal/mol respectively.[116] The standard deviation for the heat of protonation of EMA was determined by taking the individual deviations from the mean ΔH_{MA} and dividing by the number of observations.

Energy changes for the complexation reactions are displayed in Table IX. These changes in calories were calculated from equations 9.1, 9.2, and 9.3. A distinctive feature of the table is the large energy changes for copper. It has the largest negative energy change for dilution of the metals studied, and the largest positive energy change

TABLE VII

EQUILIBRIUM CONSTANTS AND CONCENTRATION DATA FOR ETHYLENE-MALEIC ACID

Ion, M^{n+}	K_{MA}	$C_M \times 10^3$, F[a]	$C_A \times 10^3$, F[a,b]	$\Delta[H^+]$ x 10^5F	$\Delta[H_2A]$ x 10^3F	$\Delta[MA]$ x 10^3F
Mn^{2+}	6.41×10^8	2.71	9.34	8.52	2.28	1.47
		2.71	9.34	9.98	2.54	1.30
		2.71	9.34	9.96	2.54	1.31
Co^{2+}	4.29×10^8	2.70	9.63	9.35	2.45	1.11
		2.70	9.63	9.74	2.52	1.07
		2.70	9.63	8.27	2.25	1.24
Ni^{2+}	3.76×10^8	2.70	10.2	8.43	2.29	1.11
		2.70	10.2	8.62	2.36	1.06
		2.70	10.2	8.59	2.34	1.08
Cu^{2+}	4.45×10^{10}	3.39	10.2	55.93	3.06	2.47
		3.39	10.2	51.88	2.96	2.56
		3.39	10.2	62.81	3.20	2.34
Zn^{2+}	4.97×10^8	2.96	9.33	9.25	2.47	1.31
		2.96	9.33	9.25	2.47	1.31
		2.96	9.33	8.34	2.29	1.47
		2.96	9.33	9.23	2.48	1.32
H^+(1st)	1.32×10^{-5}	2.96	9.33	6.86	2.66	2.72
H^+(2nd)	2.87×10^{-10}	2.96	9.33	28.93	2.64	2.70

a C_M,C_A are final analytical concentrations
b Final volume = 33.36 ml for metals
Final volume = 32.48 ml for $HClO_4$

energy change for dilution of the metals studied, and the largest positive energy change during complex formation. The probable reasons for these extremes will be discussed later. The heats of formation were calculated from the energy changes.

TABLE VIII

HEAT OF PROTONATION OF EMA

Ion, M	Heat Capacity, $\bar{h}$, cal/cm	Deflection, D, cm	Q_{H_2A} 10^2 cal	ΔH_{MA} Kcal/mol	Mean H_{MA}[a]
H^+	0.033	0.83	-2.76	-0.32	
	0.033	0.55	-1.82	-0.21	
	0.028	0.56	-1.57	-0.18	-0.24 ± 0.07

a Error expressed as standard deviation

The heats of formation for the transition metal-EMA complexes of manganese, cobalt, nickel, copper, and zinc are given in Table X. These heats of formation range from -0.97 to 3.61 kcal/mol for nickel and copper respectively. The error for the heats is expressed as the standard deviation. Again the standard deviation was calculated by taking the individual deviations from the mean ΔH_{MA} and dividing by the number of observations taken for each metal. The magnitude of the errors range from 6% for cobalt to 17% for zinc which are well within acceptable limits for experimental errors.

TABLE IX

ENERGY CHANGES FOR METAL-EMA COMPLEXATION

Ion, M^{2+}	Heat Capacity $\bar{h}$, cal/cm	Deflection D, cm	Q_E, 10^2 cal	Q_{MA}, 10^2 cal	Q_{H_2A}, 10^2 cal	Q_{DIL}, 10^2 cal
Mn	0.032	1.48	4.73	8.48	−1.83	−1.92
	0.031	1.45	4.49	8.42	−2.01	−1.92
	0.032	0.96	3.08	7.25	−2.25	-1.92
Co	0.030	2.78	8.34	−2.90	−1.94	+13.2
	0.030	2.73	8.20	−3.00	−2.00	+13.2
	0.031	2.71	8.40	−3.33	−1.78	+13.2
Ni	0.022	3.01	6.63	−3.44	−1.83	+11.9
	0.024	2.88	6.91	−3.11	−1.88	+11.9
	0.025	2.41	6.03	−4.00	−1.87	+11.9
Cu	0.026	9.00	23.4	31.3	−2.43	−5.76
	0.022	8.02	17.6	28.6	−2.34	−5.76
	0.023	10.30	23.7	31.5	−2.54	−5.76
Zn	0.026	2.90	7.55	12.50	−1.94	−3.01
	0.027	1.67	4.50	9.45	−1.94	−3.01
	0.032	1.71	5.47	10.06	−1.58	−3.01
	0.034	2.11	7.17	12.13	−1.95	−3.01

TABLE X

HEATS OF COMPLEXATION OF METAL-EMA

Ion, M^{2+}	ΔH_{MA} Kcal/mol	Mean ΔH_{MA} Kcal/mol[a]
Mn	1.73	
	1.94	
	1.61	
		1.76 ± 0.14
Co	-0.78	
	-0.84	
	-0.81	
		-0.81 ± 0.05
Ni	-0.93	
	-0.88	
	-1.11	
		-0.97 ± 0.12
Cu	3.80	
	2.99	
	4.03	
		3.61 ± 0.51
Zn	2.97	
	2.17	
	2.26	
	2.75	
		2.54 ± 0.43

a Error expressed as standard deviation

Values for ΔG_{MA}, ΔH_{MA}, and ΔS_{MA}, calculated from the Gibbs free energy equation, are given in Table XI, together with the literature values for the corresponding metal monosuccinates.[99] The comparison of the polymeric and monomeric analogs show that the enthalpies of complex formation defined in terms of a monomeric unit of

TABLE XI

COMPARISON OF THERMODYNAMIC PARAMETERS OF M-EMA AND M-SUCCINATE COMPLEXES

	M-EMA			M-Succinates[99]		
Ion	$-\Delta G$, Kcal/mol	ΔH, Kcal/mol	ΔS, eu	$-\Delta G$, Kcal/mol	ΔH, Kcal/mol	ΔS, eu
Mn	12.05	1.76	46.3	3.09	3.02	20.5
Co	11.75	−0.81	36.8	3.02	3.15	20.7
Ni	11.99	−0.97	36.8	3.20	2.46	19.0
Cu	14.53	3.61	60.9	4.42	4.56	30.1
Zn	11.88	2.54	48.4	3.36	4.39	26.0
H(1st)[a]	6.63	−0.24	21.4	5.75	−0.76	16.8
H(2nd)[a]				7.59	−0.06	25.6

a Values are for protonation rather than ionization

ligand are less endothermic than the values for the monosuccinate complexes which could be considered to be the monomeric analogs. For example, for the copper complexes the heats of formation are 3.61 kcal/mol for EMA and 4.56 Kcal/mol for succinic

acid. By analogy, therefore, one could conclude that the metals are bound to the polyion at specific sites. In the process, substitution into the coordination sphere of the metal ion has occurred. This change in ΔH_{MA} to a more favorable value does not exclusively account for the extreme stability of the metal-EMA complexes over the monosuccinates.

It should be emphasized that the entropy contribution is much more favorable to the overall stability causing an increase in $T\Delta S$ on the order of 4.8 to 9.2 kcal/mol. If it is assumed that the increase in entropy caused by the release of solvent bound to the metal is constant for monomer and polymer, the effect of a structural or conformational change of the polyion must be considered. This is especially important since the chelate effect is small for a seven-membered ring.

The partial neutralization of the polyacid results in a progressive buildup of negative charge and produces extension of the chain by increasing the end to end distance. This results in an extensive ordering of the immediate solvent structure[70] and a corresponding decrease in entropy. The metal ion interactions also contribute to the entropy decrease.

Consideration of the changes in ΔH_{MA} would indicate that the metal ions are more tightly bound to the polymer at the specific sites than is possible in the monomeric analog. This result would have far-reaching effects on the solvation of the metal ions when bound, perhaps accounting for a small increase in entropy. It may be concluded that this small secondary entropy increase is fairly constant since the variation in ΔH_{MA} from metal to metal is comparable to the monosuccinate case. These similarities suggest that the contribution of the metals to the various heats of formation may be constant.

As explained previously, the EMA heat of protonation, HA^-, was not unusual when compared to values for simpler monomeric acids;[114] e.g., ΔH_{HA^-} for succinic acid is −0.76 kcal/mol and the heat of protonation for EMA as determined in this study is −0.24 kcal/mol. The present value for EMA is perhaps best considered to be an average value. For example, it is instructive to observe that the average ΔH of protonation of citric

acid[90] is −0.26 kcal/mol. These comments are equally valid for the entropies of protonation (Table XI).

It is therefore proposed that the structure of the partially neutralized acid in the first ionization process is an elongated chain in which the vicinal carboxylic acid groups are linked by intramolecular hydrogen bonds. When the hydrogen bonds are opened, with the release of protons, strong metal interactions occur at the specific sites. The polyion may then adopt a more rigid conformation in which hydrophobic contacts are produced. Any loss in entropy from additional proton solvation and the change in conformation is nevertheless exceeded by the gain in entropy realized by the liberation of ordered solvent molecules as the metal ions and the polymer are complexed.

Summary of Results for Transition Metal Ethylene-Maleic Acid Study

Three specific observations are worthy of further comment. Copper appears to undergo a change in coordination number on complexation.[99] This may account for the much more endothermic ΔH_{MA} and much more favorable entropy change. The most endothermic changes are for Zn^{2+} and Cu^{2+}, both of which have tetrahedral geometry (if the above interpretation for Cu^{2+} is valid). This may reflect the increasing strain introduced in the ligand molecule in bonding with these ions.

Second, for the relative magnitudes of ΔH_{MA} from metal to metal, the variation is similar to the monosuccinate case which suggests that the role of the metal is constant.

Finally, as noted in Chapter VII, there is little correspondence with results from other systems; e.g., copper polyacrylate,[98] ΔH_{MA} = 0.5 kcal/mol and ΔS_{MA} = 28 eu; but, this may be a consequence of the experimental limitations of the temperature dependence method. It is conceivable, for example, that conformational changes of the polymer with temperature may substantially change the heat capacity of the process.

This study then has shown that 1) the heats of association of polymers and metals can

be determined calorimetrically, 2) the metal-EMA heats are less endothermic than the corresponding monomeric analog - succinic acid, 3) the previously determined free energies of association can be used to determine the entropies of association, 4) the determined entropies are large and positive, and 5) the large entropies may be because of solvent liberation from the polyion EMA and the metal ions during complexation.

CHAPTER XI

RECOMMENDATIONS FOR FURTHER METAL ETHYLENE-MALEIC ACID STUDIES

To provide an insight into the binding of metals other than the transition metals, the association constants and the heats of formation for Group I and Group II metal ions with ethylene-maleic acid should be determined. The heats of formation measurements will determine if the reaction is enthalpy or entropy driven. If the EMA-alkali and EMA-alkaline earth complexes are strong enough, this extension of the study opens up the potential for using polyelectrolytes in a desalination process analogous to the pollution abatement process proposed for transition metal complexes.[114]

Also work should be done to determine the effectiveness of EMA to complex with transition metals when brines with 10,000 ppm or greater total dissolved solids are present. This work might be helpful to breakdown metal-crosslinked polymers such as polyacrylamides in oilfield applications.[117]

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APPENDIX

Description of Computer Programs

Three Fortran computer programs were used on the IBM 370, Model 168, computer at Amoco Production Company Research Center. They included a linear least squares program to determine the independent variables which influence the gel times, another linear least squares program to determine the coefficients for a multiplied power law kinetic model and a set of statistical analysis programs which plotted the data. The first two programs were modified from programs obtained from the Tulsa Research Center of Amoco Production Company. The third program was purchased by Amoco Production Company from SAS Institute Inc., Chapel Hill, North Carolina. The programs were compiled and stored on a disk memory unit.

Determination of Independent Variables

The program SOLVE determines the independent variables by a linear least squares analysis of the data. The data are fit to the equation

$$\ln(\text{gel time}) = Aa * Bb * c/\text{temperature} + D \qquad \text{(A-1)}$$

where A is the reducing sugar content as a result of the pulping process, B is the weight fraction of the lignosulfonate, D is the proportionality constant relating gel time to rate, and a, b, and c are related to to the input parameters.

The program SOLVE uses a free format input which simplifies data input. The data set is entered as follows:

Line 1

READS IN THE NUMBER OF DATA SETS

Line 2

READS NUMBER OF VARIABLES & POINTS TO BE ANALYZED

Line 3

READS IF THE DATA IS TO BE CENTERED, 0 = No, 1 = Yes

Line 4

READS THE NUMBER OF SQUARED TERMS, n

Line 5 to n

READS THE SQUARED TERMS

Let 5 + n + 1 = A

Line A

READS THE NUMBER OF SECOND ORDER INTERACTION TERMS, n'

Line A + 1 through A + n'

READS THE SECOND ORDER INTERACTION TERMS

Let A + 1 + n' = B

Line B

READS THE NUMBER OF THIRD ORDER INTERACTION TERMS, n"

Line B + 1 through B + n"

READS THE THIRD ORDER INTERACTION TERMS

Let B + 1 + n" = C

Line C

READS THE NUMBER OF FOURTH ORDER INTERACTION TERMS, m

Line C + 1 through C + m

READS THE FOURTH ORDER INTERACTION TERMS

Let C + 1 + m = D

Line D

READS THE NUMBER OF FIFTH ORDER INTERACTION TERMS, m'

Line D + 1 through D + m'

READS THE FIFTH ORDER INTERACTION TERMS

Let D + 1 + m' = E

Line E + number of data points

READS THE INDEPENDENT AND DEPENDENT VARIABLES

All data is now entered.

The program begins the calculations by taking the natural log of the gel time and converting the temperature to degrees Kelvin. It reads the input data, calculates the appropriate interaction terms (i.e., if second order interactions are input it will multiply the terms input as these interactions), sets up the normal equations, solves the equations by Gaussian elimination, calculates the sum of squares of the residuals, the mean square of the residuals, determines the overall standard deviation, and degrees of freedom, and prints the results of the analysis.

After solving the matrix of the normal equations by Gaussian elimination, the program calls a routine to invert the normal equation matrix. The coefficients for the variances and covariances and correlation coefficients of the dependent variables are calculated from the elements of the inverted matrix.

After returning to the MAIN program the results are printed as correlation coefficients between each variable, the standard deviations for each variable.

To load this program into memory an executive program called SOLVE was written. Some functions of an executive program are to 'manage' terminal communications with the computer and/or the disk files and to manipulate disk files. In the SOLVE executive program, the input-output devices are defined. It also contains commands to load the program into memory and start the execution. This particular executive program causes the program results to be printed on the CRT. Another executive program was written which causes the results to be printed on a disk file. It is called SOLVEDISK.

Determination of Coefficients

This program named SOLVLNL calculates the coefficients for the linear form of the model

$$\ln(\text{Gel Time}) = a\ln A + b\ln B + c/\text{Temperature} + D \qquad \text{(A-2)}$$

where A is the reducing sugar content, B is the weight fraction lignosulfonate, D is the natural logarithm of the proportionality constant, and a,b, and c are the coefficients determined. The data set is entered as described above except no interactions were put into this linear model (e.g., from line 4 to line E were set equal to zero).

When the calculations are begun the natural logarithms of each variable and the gel time are taken. The reaction temperature is converted to degrees Kelvin and divided into 1000. The program then determines the coefficients of the variables by linear least squares analysis.

To access this program an executive program called SOLVLNL was written which loads it into memory from a remote CRT terminal. This executive program corresponds to the SOLVE executive program except it loads SOLVLNL for execution not SOLVE.

Data Plots

The programs which were used to plot the data were called from the Statistical Analysis System (SAS). These programs could also be used to determine the coefficients and the components which most affect the gel times. However, it does not have a matrix inversion routine which is as efficient as SOLVE or SOLVLNL. Because of this SAS was only used to plot the data and to run an F-test of the variables.

From the plots generated in this program the reaction orders could be determined by subtracting the temperature, the reducing sugar, or the lignosulfonate effects respectively.

The F-distribution tests showed that the reducing sugars and the lignosulfonate weight fraction are variables in the lignosulfonate liquors which influence the gel times.

VITA

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Doctor of Philosophy

Thesis: FACTORS AFFECTING THE KINETICS OF GELATION OF LIGNOSULFONATE AND THE MEASUREMENT OF THE HEATS OF ASSOCIATION OF TRANSITION METAL COMPLEXES OF ETHYLENE-MALEIC ACID

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